VOL. XXX 1916

TRANSACTIONS

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OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

VOLUME XXX

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THIRTIETH GENERAL MEETING

NEW YORK CITY, SEPTEMBER 27, 28, 29, 30, 1916

PUBLISHED BY

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AT THE OFFICE OF ITS SECRETARY

LEHIGH UNIVERSITY, SOUTH BETHLEHEM, PA.

1917

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VOLUME XXX 1916

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

PROCEEDINGS

CONDENSED MINUTES OF THE THIRTIETH GENERAL MEETING OF THE SOCIETY, HELD IN CONNECTION WITH THE SECOND NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES, IN NEW YORK CITY, SEPTEMBER 27, 28, 29, 30, 1916.

Number of members registered, 216; number of guests registered, 281; total, 497.

PROCEEDINGS OF WEDNESDAY, SEPTEMBER 27

Registration began at the entrance of the Chemical Exposition, and also at the Hotel Astor.

This being "Electrochemical Day" at the Exposition, the opening assembly was held in the Exposition building at 11.00 A. M. Dr. C. G. Fink, Chairman of the New York Section of the Society, presiding. Mr. Adriaan Nagelvoort, manager of the Chemical Exposition, welcomed the members, and an address by President F. A. J. FitzGerald was read by Dr. J. A. Mathews, Mr. FitzGerald unfortunately being detained at Niagara Falls by illness. President FitzGerald's address was as follows:

When I emigrated to the United States nearly a quarter of a century ago I was immensely struck with the great stress laid on the word "imported" when buying anything. The excellence of the goods would be freely explained by the salesman, but he generally reached a climax when he pointed out that they were "imported."

Before coming to this country I do not remember observing

that excessive modesty was a characteristic of its citizens and yet the enormous respect paid to imported goods seemed to imply its existence.

Here, as everywhere else, we find that we can do better in many cases by using articles manufactured in other countries, but the mere fact of being imported is hardly a proper recommendation. Some years ago when in Germany I visited a large steel plant where the guide apologized for some rather antiquated rolling-mill machinery which he showed me, but when we had looked at this he conducted me with pride to another mill where he said they had American machinery or at least machinery of American design. Again, you may see shoe factories in England which are said to be very efficient establishments because they have American machinery. And so in various European countries you will find things are represented as having certain excellent qualities because they come from some place where such articles have a well-deserved reputation, but I do not remember having ever heard of a thing being recommended just because it was imported.

Now the existence of an idea that because something is imported it must be of greater excellence obviously involves the tacit assertion that things made in this country are inferior. This attitude towards imported articles has, I think, been considerably modified in recent years, and as a means of bringing about this desirable modification, exhibitions such as this of our chemical industries are of immense value.

When the United States were sparsely inhabited and there were relatively few industries, they had to depend for many things on importation, and so it came about that an indiscriminating belief in the excellence of imported articles developed and this as regards many of these things exists even today.

Certainly in such matters it is not desirable to attempt to develop any spirit of nationalism which would induce us to support a home product which is inferior to the imported, but it is always well, even from a purely selfish point of view, to investigate what can be done at home before going abroad, and even if the home product is inferior to try and find the cause of its inferiority and then if possible to assist that industry to equal or excel the foreign product. Here again we find a valuable function of a national exposition such as this.

In various industries the United States is now in a position where it is well to the front or actually leader and I think we may assert without fear of contradiction that the electrochemical industry is one of these. The field is comparatively new and we did not start in it with the handicap which existed in many of the older industries. In certain industries covered by the general term electrochemical we certainly have the foremost place—for example, in the manufacture of artificial abrasive materials. In other cases (such as the application of the electric furnace to steel) we have lagged behind until recently. Again in others we are a long way behind developments in Europe, as in the fixation of atmospheric nitrogen.

It is well worth while studying those subjects in which we are not and have not been in the front rank in order to determine why this is so. Thus a study of the development of the use of the electric furnace for the manufacture of steel seems to show that special conditions in Europe tended to stimulate the development there and that it was actually to our advantage that the pioneer work should be done there rather than here so that we have no cause to regret that while the pioneer work in this branch was being done in Europe we were busy in other directions.

On the other hand, the study of the development of electrochemical methods of nitrogen fixation shows a different reason for our backward position. Those not conversant with electrochemical history are apt to believe that this is altogether a foreign development, never having heard of the work of Bradley and Lovejoy at Niagara Falls more than twelve years ago. Here then we had a remarkable development that was arrested because of adverse environment. For in Europe when similar developments took place it was possible to obtain abundance of cheap electric power. When the question of "National Preparedness" is in everyone's mind we are asked what is to be done about the preparation of nitrates, for in this respect we are by no means ready, and the Committee on Public Relations of the American Electrochemical Society in its report to the administration on this subject recommends "a liberal water power policy, as the question of the cost of power is vital to several of the processes."

These examples show the value of a study of our position in the electrochemical industry and similar studies in other fields

should also give profitable results. The electrochemist uses a great variety of materials and articles: chemicals, physical apparatus, electrical machinery, etc., some made in America, others abroad. It was with this in mind that the Electrochemical Society decided that at its meeting held here at the same time as this great National Exposition of Chemical Industries it would be of interest and value to devote a whole session to the subject "Made in America" as related to electrochemical interests.

This discussion of the subject should be useful in several ways. It may help to develop a more critical study of imported materials and articles, and this is very necessary, for it is a fact that we are often apt to be less critical of an imported than of a domestic article, and there can be no doubt that the foreign manufacturer often likes to unload on us materials which he could not sell at home.

As an example of this I may mention the advice I received from an eminent American physicist who gave me the address of the well-known German manufacturer of thermometers; said he, "When you place your order tell him that you know what good thermometers are and that you don't want him to send any of the poor quality which German manufacturers think are quite good enough for American consumption."

In other words the discussion of "Made in America" will stimulate a more discriminating appreciation of imported articles.

Another useful end will be served if the discussion of it reveals why the domestic product does not give the satisfaction which the imported material does. This may develop much needed co-operation of the consumer and the producer. There has not been enough of this. If the domestic article is not satisfactory the consumer has been in the habit of throwing it out and using the imported article without having sufficiently long sight to see that it was worth while to co-operate with the producer in helping him to better his manufacture.

It is perhaps getting dangerously near a political question, which ought not to be political, to say that mutual co-operation of producer and consumer is in the long run of far more importance than protection, which is sometimes apt to encourage the manufacture of inferior articles.

Perhaps, then, one of the greatest uses of such an exhibition

as this is the way in which it brings together the manufacturer and the consumer to their mutual benefit and for this we surely owe a great debt of gratitude to those responsible for it.

The rest of the day was devoted to inspection of the exposition.

The ladies were taken an automobile tour along the Hudson under the chaperonage of Mrs. J. M. Matthews.

The Board of Directors and the Publication Committee held a meeting in the evening at the Hotel Astor.

PROCEEDINGS OF THURSDAY, SEPTEMBER 28

A meeting for the reading and discussion of papers was held in the Hotel Astor, commencing at 9.30 A. M. The general topic of this session was "Made in America," a symposium arranged and conducted by Mr. L. E. Saunders, to enlarge upon the ability of America to manufacture for herself the many articles formerly imported.

The discussion was opened by Mr. Saunders, continued by Mr. Acheson Smith of Niagara Falls, Dr. Edw. Schramm of the Bureau of Standards, and again by Mr. Saunders. Discussion was active, being participated in by numerous members and guests, as published in full in these Transactions.

Luncheon was taken at the Hotel Astor, and the afternoon session was opened at 2.30 P. M. with the reading and discussion of papers, by the following: O. P. Watts and P. L. DeVerter (read by title), E. A. and L. T. Richardson (read by title), O. C. Ralston and C. E. Sims (read by title), H. J. Morgan and O. C. Ralston (read by title), S. Fischer (read by title), L. D. Hammond (read by title), F. C. Mathers and F. G. Sturdevant (read by title), W. Blum, H. D. Holler and H. S. Rawdon (presented by Mr. Blum). These papers and their discussion are printed in full in these Transactions.

In the evening a smoker was held in the grand ballroom of the Hotel Astor to which were invited as guests of the Society the members of the American Chemical Society, present at their meeting in New York City. The smoker was attended by eight to nine hundred members and guests and was a most notable event in the doings of a very busy week.

PROCEEDINGS OF FRIDAY, SEPTEMBER 29

A meeting for reading and discussion of papers was held at 9.30 A. M. at the Hotel Astor. Papers were read and discussed as follows: C. F. Burgess (abstracted and presented by Mr. W. B. Schulte), L. C. Turnock (abstracted by Secretary Richards), Carl Hering, F. A. Fahrenwald (abstracted by Assistant Secretary Roush), T. H. Leaming, H. Schlundt and Julius Underwood (read by title), M. J. Brown, Grinnell Jones and M. L. Hartman (abstracted by Secretary Richards). These papers and discussions are printed in full in these Transactions.

Dr. Carl Hering offered the following motion which was seconded and unanimously passed: "The American Electrochemical Society, at the close of its Thirtieth General Meeting, wishes to place on record its grateful appreciation of the co-operation and assistance of the following, towards the success of this meeting and the pleasure and profit of the members and guests in attendance.

The Board of Directors of the Second National Exposition of Chemical Industries, for accommodation in holding the opening session.

The Management of the Hotel Astor for accommodation as to meetings and registration.

The Bureau of Standards, Washington, for active participation in the 'Made in America' session.

The American Chemical Society, for reciprocal courtesies in connection with entertainment of visiting members and guests.

The Local Committee of the Society and its Sub-committees, in particular the Ladies' Committee, for their exceedingly active and efficient service in arranging a multitude of details and functions which have contributed greatly to the pleasure and profit of the members and guests in attendance."

After luncheon at the Hotel Astor the afternoon was devoted to inspection of the Exposition of Chemical Industries. In the evening members of the Society were invited to join the members of the American Chemical Society in a subscription banquet at the Waldorf-Astoria Hotel. The banquet was a great success and very pleasantly closed the week's proceedings.

PROCEEDINGS OF SATURDAY, SEPTEMBER 30

The day was devoted to a complimentary excursion up the Hudson as far as West Point and return, which was numerously attended by members and guests of the Society and of the American Chemical Society, giving a fine opportunity for personal acquaintance and conversation upon the scientific proceedings of the week.

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ABBOTT, William G. Jr. (Mar. 27, '09) care of Hillsboro Mills, Wilton, N. H.
ACHESON, E. G. (Apr. 3, '02) Acheson Corp., Aeolian Bldg., 35 W. 42d St., New York City.
ACKER, Charles E. (Apr. 3, '02) President, The Nitrogen Co., Ossining-on-Hudson, N. Y.
ACTON, E. H. (Oct. 23, '14) Supt., Northern Aluminum Co., Shawinigan Fall, P. Q., Canada.
ADAMS, James L., Jr. (June 2, '16) 420 Montview Place, Wilkinsburg, Pa.
ADAMS, Quinton (July 28, '16) Elec. Eng., 1st National Bank Bldg., 1 Montgomery St., San Francisco, Cal.
ADAMS, Thos. J. (Aug. 25, '16) Res. Asst., Aluminum Co. of America, Maryville, Tenn.
ADAMSON, G. P. (Dec. 4, '02) Gen. Mgr., Baker & Adamson Chem. Co.; res., 233 Reeder St., Easton, Pa.
ADDICKS, Lawrence (Apr. 3, '02) Consulting Eng., Room 2, 126 Liberty St., New York City.
ADSIT, Charles G. (Sept. 26, '08) 1 Ponce de Leon Ave., Atlanta, Ga.
AHLBRANDT, G. F. (Jan. 29, '09) Asst. Gen. Sales Mgr., Amer. Rolling Mills, Co., Middletown, Ohio.
AIKEN, Robert H. (Oct. 10, '03) Metallurgist, Winthrop Harbor, Ill.
ALBRIGHT, Langdon (Sept. 26, '08) 1st Vice-Pres., Ont. Power Co., 1608 Marine Bank Bldg., Buffalo, N. Y.; res., 33 Oakland Place.
ALDRICH, Chas. H. (July 25, '13) Metallurgist, Colgate, Baltimore County, Md.
ALDRIDGE, Walter H. (Jan. 28, '08) 14 Wall St., New York City.
ALEXANDER, C. M. (Sept. 27, '16) Res. Chemist, Gulf Ref. Co., Port Arthur, Texas.
ALEXANDER, H. H. (July 25, '13) Mgr., American Smelt. and Ref. Co., Perth Amboy, N. J.; res., Maurer, N. J.
ALLEMAN, Gellert (Jan. 28, '11) Professor of Chemistry, Swarthmore College, Swarthmore, Pa.
ALLEN, Herbert I. (July 25, '13) 286 State St., Portland, Me.
ALLEN, O. F. (Oct. 21, '16) Sales Eng., General Elec. Co., Room 1712, 30 Church St., New York City.
ALLYN, R. S. (Feb. 5, '03) Patent Lawyer, 16 Exchange Place, New York City, res., 24 Irving Place, Brooklyn, N. Y.
AMBERG, Dr. Richard (Mar. 26, '10) Schwerte i. W., Germany.
AMER, Henry S. (May 27, '11) Assistant in Eng. Dept., Westinghouse Lamp Co., Bloomfield, N. J.; mailing address, 14 Evergreen Ave.
AMINOFF, Gustav (Feb. 27, '09) Abo Vuoksenniska (Finland) Russia.
AMSTER, N. L. (Apr. 3, '02) Consult. Min. Eng., 32 Equitable Bldg., Boston, Mass.
ANDERSON, Chas. E. (Sept. 27, '16) Gen. Mgr., Smuggler Leasing Co., Aspen, Colo.
ANDREWS, Joseph C. (May 26, '10) Chief Chemist, American Hardware Corp., New Britain, Conn. Mailing address, 123 Vine St.
ANDREWS, Wm. S. (April 6, '11) Consulting Eng., General Electric Co., Schenectady, N. Y.; res., 136 Park Ave.
ANTISELL, Frank L. (July 25, '13) Asst. Supt., Raritan Copper Works, Perth Amboy, N. J.
ANTUNEZ, Vicente (June 30, '16) Miner, 325 Merced, Santiago, Chile.
APPEL, Moses (Apr. 6, '11) 118 Walnut St., Johnstown, Pa.
ARISON, William H. (July 31, '08) Mgr., Int. Acheson Graphite Co., Niagara Falls, Ont., Canada.
ARMES, Henry P. (Jan. 27, '12) Lecturer in Chemistry, University of Manitoba, Manitoba, Winnipeg, Canada.
ARMSTRONG, Lyndon K. (Aug. 27, '09) Mining Engineer, Spokane, Washington. mailing address, P. O. Drawer 2154, Spokane, Wash.
ARNEMANN, Dr. Paul (Apr. 29, '11) Grindelhof 19, Hamburg 13, Germany.
ARSEM, William C. (Nov. 27, '09) Chemical Engineer, General Electric Co., Schenectady, N. Y.; res., 10 Waverly Place.

ARTHUR, Walter (Apr. 27, '12) Chemist and Met. Eng., Frankford Arsenal, Philadelphia, Pa.
ASEF, Dr. Waldemar (Oct. 21, '16) Res. Chem., Penna. Salt Mfg. Co., Greenwich Point, Philadelphia.
ASHCROFT, Edgar A. (May 1, '06) 65, London Wall, London, E. C., England.
ASKENASY, Paul, Ph. D. (Feb. 25. '11) Kaiser Allee 20, Karlsruhe (Baden), Germany.
ASTON, James (Jan. 28, '08) 5826 Nicholson St., Pittsburgh, Pa.
ATWATER, C. G. (Oct. 22, '15) Mgr. of Agricultural Dept., American Coal Products Co.; mailing address, 17 Battery Place, New York City.
ATWOOD, F. C. (Sept. 27, '16) Res. Eng., The Exolon Co., Thorold, Ont., Canada.
AUSTIN, A. O. (Sept. 27, '16) Chief Eng., The Ohio Insulator Co.; mailing address, 326 North Sixth St., Barberton, Ohio.
AUSTIN, L. S. (Sept. 27, '16) 251 West 2d North St., Salt Lake City, Utah.
BABROWSKY, G. (Mar. 25, '08) Inst. for Theor. and Physical Chemistry, Ceská vysoká skola technika, Brünn, Moravia, Austria.
BACHOFNER, D. K. (March 26, '10) Assistant Superintendent, Irvington Smelting & Refining Co., Irvington, N. J.
BACON, R. F. (Nov. 28, '13) Associate Director Mellon Inst., Univ. of Pittsburgh, Pittsburgh, Pa.
BADGER, A. C. (Sept. 27, '16) Chemist and Met., Briscoe Motor Corp., Jackson, Mich.
BAEKELAND, Dr. Leo H. (Jan. 6, '03) "Snug Rock," Harmony Park, Yonkers-on-Hudson, N. Y.
BAILEY, Richard O. (Oct. 21, '16) Chemist, Oneida Community Ltd., Oneida, N. Y.
BAILY, Thaddeus F. (Feb. 25, '11) Gen. Mgr., The Electric Furnace Co. of America, Alliance, Ohio.
BAIN, J. Watson (Oct. 27, '11) Associate Prof. of Applied Chemistry, C. & M. Bldg., The University, Toronto, Canada.
BAJDA, Jas. J. (Sept. 27, '16) Gen. Supt., B. Heller & Co., Chicago Heights, Ill.; mailing address, 7514 Parnell Ave., Chicago, Ill.
BAKER, Chas. E. (Aug. 5, '05) Metallurgist, 201 Traders Bldg., Chicago, Ill.; mailing address, 324 Postal Bldg., La Salle and Van Buren Sts., Chicago, Ill.
BAKER, E. M. (Apr. 26, '16) Chemist, Hooker Electrochemical Co., Niagara Falls, N. Y.; mailing address, 351 Sixth St.
BAKER, Herbert A. (Dec. 27, '07) Chemist, care of the American Can Co., 447 W. 14th St., New York City.
BAKER, John T. (Mar. 30, '08) Phillipsburg, N. J.
BAKER, L. R. (Mar. 24, '16) Mgr., Canada Dry Cells Ltd.; mailing address, Oakview Ave., East Kildonan, Manitoba.
BAKER, Robt. E. (Jan. 22, '15) Wks. Mgr., Keokuk Electro-Metals Co.,; mailing address, 526 N. 4th St., Keokuk, Iowa.
BALDWIN, Allen T. (Dec. 31, '15) Chem., Manhattan Elec. Supply Co., 41-47 Morris St., Jersey City, N. J.
BALTZELL, Willie H. (May 27, '11) Canadian Steel Corp. Ltd., Ojibway, Ontario, Canada.
BANCROFT, Wilder D., Ph. D. (Apr. 3, '02) Cornell University; res., 7 East Ave., Ithaca, N. Y.
BARCLAY, Earle H. (Oct. 21, '16) Res. Eng., Aluminum Co. of America, Niagara Falls, N. Y.
BARKER, E. R. (Apr. 3, '02) 79 Milk St., Room 1110, Boston, Mass.
BARNES, H. H., Jr. (June 30, '16) District Eng., General Elec. Co.; mailing address, 32 W. 40th St., New York City.
BARNES, W. A. (Apr. 26, '13) Clift Hotel, San Francisco, Cal.
BARNHILL, W. J. (Sept. 27, '16) Owner Chem. Labs.; mailing address, P. O. Box 306, Colton, Cal.
BARR, Harry L. (Oct. 21, '16) Chem. and Asst. Elchem., Follansbee Bros. Co., 125 N. High St., Steubenville, Ohio.
BARRE, H. A. (May 5, '10) Elec. & Mech. Eng., Pacific Lt. & Power Corporation, 649 Pacific Electric Bldg., Los Angeles, Cal.
BARROWS, F. E. (Aug. 22, '13) Patent Attorney, 35 Nassau St., New York City.
BARROWS, W. S. (Apr. 26, '13) Foreman Electro-plater, Russell Motor Car Co.; res. 628 Dovercourt Road, Toronto, Ont., Canada.
BARSTOW, W. S. (Apr. 3, '02) 56-58 Pine St., New York City.
BARTON, Charles B. (Sept. 4, '02) Burgess Sulphite Fibre Co., Berlin, N. H.
BARTON, P. P. (Feb. 2. '06) Gen. Mgr., Niagara Falls Power Co., 352 Buffalo Ave., Niagara Falls, N. Y.
BARTON, W. H. (Feb. 25, '11) Met. Chemist, Searchlight, Nev.
BARWICK, William S. (Dec. 31, '09) Chemist and Metallurgist, Vancouver Engineering Works, Vancouver, B. C., Canada; mailing address, Charpole Ave.
BASKERVILLE, Chas., Ph. D. (Apr. 4, '03) Prof. of Chem., College City of New York, New York City.
BASSETT, Wm. H. (Nov. 26, '07) Technical Supt. and Metallurgist, The American Brass Co., Waterbury, Conn.; res., Cheshire, Conn.
BATCHELDER, John K. (Apr. 2, '13) Foreman, Electrolytic Zinc Plant, Consolidated Mining and Smelting Co. of Canada, Ltd., Trail, B. C., Canada.

BATE, H. A. (Sept. 27, '16) Metallurgist., Res. Dept., American Rolling Mill Co., Middletown, Ohio.
BAUER, G. W. (Sept. 4, '03) Vice-Pres. and Chem., Bauer, Schweitzer Hop and Malt Co., 1722 Buchanan St., San Francisco, Cal.
BAUER, Wm. Chas. (May 27, '11) Professor of Electrical Engineering, Northwestern University, Evanston, Ill.; res., 2149 Sherman Ave., Evanston, Ill.
BAYARD, R. A. (Apr. 24, '14) Resident Supt., Chippewa Plants, Norton Co., Chippewa, Ont.; mailing address, 170 Buffalo Ave., Niagara Falls, N. Y.
BEAR, S. L. (Feb. 26, '15) Gen. Eng., West. Elec. & Mfg. Co., 4001 Northminster St., North Side, Pittsburgh, Pa.
BECK, Dr. Erick A. (Apr. 29, '11) Metallurgist, Goldschmidt Thermit Co., 120 Broadway, New York City; res., 931 Park Ave.
BECKET, Frederick M. (Apr. 3, '02) The El.-Met. Co. of America, 403 Jefferson Ave., Niagara Falls, N. Y.
BECKMAN, John Woods (May 6, '05) Beckman & Linden Engineering Corp., Balboa Bldg., San Francisco, Cal.
BEDELL, E. H. (Oct. 22, '15) Advertising Solicitor, McGraw-Hill Pub. Co., 239 W. 39th St., New York City.
BENECKE, Adelbert O. (Sept. 26, '08) 3 Rock Ave., Swampscott, Mass.
BENNETT, Benjamin F. (Feb. 26, '10) care of American Sheet & Tin Plate Co., 1328 Frick Bldg., Pittsburgh, Pa.
BENNETT, C. W. (Mar. 23, '12) Asst. Prof. of Chem. Eng., Cornell University, Ithaca, N. Y.; mailing address, 436 N. Geneva St.
BENNETT, M. H. (Nov. 28, '13) Res. Engineer, 26 Linden St., Waterbury, Conn.
BENOLIEL, Sol. D., B. S., E. E., A. M. (Sept. 4, '02) Gen. Mgr. International Chem. Co., Camden, N. J.; mailing address, 4508 Locust St., Philadelphia, Pa.
BERG, E. J., Dr. (Oct. 2, '02) Union Univ., Schenectady, N. Y.
BERGEN, R. C. (Oct. 22, '15) Asst. Editor, Met. and Chem. Eng., 239 W. 39th St., New York City.
BERGLUND, Edw. S. (Aug. 30, '12) Manager and Chief Engineer, Trollhättan Elekthermiska Aktiebolag, Trolhättan, Sweden.
BERRY, Edw. R. (Dec. 1, '06) Chief Chem., Eng. Lab., Gen. Elec. Co., Lynn. Mass.; res., 30 Hancock St., Malden, Mass.
BERTHIER, U. H. (Sept. 27, '16) 1738 Carrollton Ave., New Orleans, La.
BETTS, Anson G. (Apr. 3, '02) care of Anson G. Betts & Co., 519 Legal Bldg., Asheville, N. C.
BIERBAUM, Christopher H. (Apr. 3, '02) Consulting Engineer, 1011 Mutual Life Bldg., Buffalo, N. Y.
BIGELOW, S. Lawrence, Ph. D. (May 9, '03) Prof. of Gen. and Phys. Chem., Univ. of Mich.; res., 1520 Hill St., Ann Arbor, Mich.
BIJUR, Joseph (Sept. 19, '03) Bijur Motor Lighting Co., River Front and 15th Sts., Hoboken, N. J.
BJÖRKSTEDT, Wm. (Apr. 6, '11) Electrometallurgical Engineer, Stavanger Steel Works, Stavanger, Norway.
BJORNSON, Einar (Oct. 29, '10) Oversoiske, Christiania, Norway.
BLANCHARD, H. J. (Nov. 24, '16) Chemist and Electroplater, Wm. A. Rogers, Ltd.; mailing address, 722 7th St., Niagara Falls, N. Y.
BLEEKER, Warren F. (Nov. 27, '09) Boulder, Colo.
BLISS, Wm. L. (Mar. 23, '12) Chief Engineer, U. S. Light & Heating Co.; res., 142 Buffalo Ave., Niagara Falls, N. Y.
BLOUGH, Earl (Apr. 29, '11) Chief Chemist, Aluminum Co. of America, Parnassus, Pa.
BLUM, William (Nov. 26, '15) Associate Chemist, Bureau of Standards, Washington, D. C.
BOECK, Percy A. (Feb. 28, '08) Eastern District Mgr., Kieselguhr Co. of America, 11 Broadway, New York City.
BOERICKE, Gideon (Mar. 5, '04) Sec. and Treas., Primos Chem. Co., Primos, Delaware County, Pa.
BOESCH, John E. (Aug. 27, '09) E. E. & M. E., Cerro de Pasco Mining Co., Lima, Peru.
BOGUE, Chas. J. (Apr. 3, '02) Mfr. of Elec. Machinery, 213-215 Center St., New York City.
BOICE, Edwin N. (June 1, '15) Purchasing Agent, care of The Hanson & Van Winkle Co., 269 Oliver St., Newark, N. J.
BONINE, Chas. E. (Aug. 30, '12) Cons. Engineer, 610 Harrison Bldg., Philadelphia, Pa.; res., 4153 Leidy Ave.
BONNEVIE, Harald (Dec. 31, '14) Chief Engr. and Mgr. of Rjukan Saltpeterverk, Rjukan, Norway.
BONSIB, R. S. (Oct. 21, '16) Res. and Exp. Eng., U. S. Metals Ref. Co., East Chicago, Ind.
BOOTH, W. K. (Aug. 25, '16) Vice-Pres. in charge of Res., Snyder Elec. Furnace Co.; mailing address, 3751 Pine Grove Ave., Chicago, Ill.
BOSWELL, Walter O. (April 26, '13) Elec. Eng., Engineering Dept. Hydro-Electric Power Commission of Ont.; mailing address, 25 Roxboro St., W., Toronto, Ont., Canada.
BOVEE, Ben. A. (Feb. 26, '15) Instructor, Eng. Dept., School of Engineering; mailing address, 917 4th St., Milwaukee, Wis.

BOWMAN, C. H. (Dec. 31, '09) President, Montana State School of Mines, Butte, Mont.; mailing address, 1020 Caledonia St.
BOWMAN, Francis C. (Jan. 29, '10) Trojan, So. Dakota.
BOWMAN, Walker (Apr. 3, '02) 39 Cortlandt St., New York City.
BOYNTON, Wm. H. (Mar. 26, '15) Chemist, 1801 Linden Ave., Baltimore, Md.
BRADFORD, Robert H. (Feb. 25, '11) Professor of Metallurgy, University of Utah, Salt Lake City, Utah.
BRADLEY, D. H. Jr. (Nov. 24, '11) Consulting Engineer, Prescott, Ariz.
BRADLEY, J. C. (Nov. 26, '07) c/o American Brass Co., Waterbury, Conn.
BRADLEY, Linn (June 30, '16) Chief Eng., Res. Corp.; mailing address, 63 Wall St., New York City.
BRADLEY, Walter E. F. (June 29, '07) Tower, Madison Square Garden, 26th St., New York City.
BRADLEY, Walter M. (Apr. 3, '02) Sheffield Scientific School, Mineral Lab.; res., 520 Whitney Ave., New Haven, Conn.
BRADY, William (May 29, '09) Chief Chemist, Illinois Steel Co., Chicago, Ill.; mailing address, 7642 Marquette Ave.
BRAGG, E. B. (Feb. 25, '11) Manager, Chicago Branch, General Chemical Co., Evanston, Ill.; res., 1838 Chicago Ave.
BRANDT, M. F. (Aug. 25, '16) Res. Chem., 109 W. 10th St., Wilmington, Del.
BRAY, William C. (May 30, '08) Dept. of Chemistry, University of California, Berkeley, Cal.
BRECKENRIDGE, C. E. (Oct. 22, '15) Chief Eng., Merck & Co., Rahway, N. J.; mailing address, Jefferson Ave.
BRECKENRIDGE, J. E. (Apr. 26. '13) Chief Chemist, Am. Agric. Chem. Co., Carteret, N. J.
BREED, George (Jan. 3, '04) Consult. Eng., Witherspoon Bldg., Philadelphia, Pa.
BRENEMAN, A. A. (May 1, '06) Analyt. & Consult. Chem., 97 Water St., New York City.
BRIGGS, Frank H. (Oct. 27, '11) Vice-Pres. and Gen. Mgr., American Dynalite Co., Amherst, Ohio.
BRINDLEY, Geo. F. (Apr. 3, '02) Box 224, Gouverneur, N. Y.
BRISTOL, Wm. H. (Dec. 1, '06) Pres., The Bristol Co., Waterbury, Conn.
BROCKWAY, John P. (Sept. 27, '16) 209 Equitable Bldg., Denver, Colo.
BROOK, G. Bernard (Feb. 23, '12) Analytical Chemist, Univ. of Sheffield, St. Georges Square, Felwood, Sheffield, Eng.
BROOKFIELD, Wm. Bertin (May 26, '10) Superintendent, Melting Department, Halcomb Steel Co., Syracuse, N. Y.; res., 109 Standart St.
BROOKS, Morgan, Ph. D., M. E. (Apr. 3, '02) Univ. of Illinois, Urbana, Ill.
BROOKS, W. C. (Mar. 23, '12) Chem. Eng., National Carbon Co.; mailing address, 1472 Alameda Ave., Lakewood, Ohio.
BROPHY, Oscar (Feb. 27, '14) Chem. Engineer, Ajax Metal Co., Philadelphia, Pa ; mailing address, 1919 N. 12th St.
BROWN, C. J. (Oct. 22, '15) Secretary, Wilson-Maeulen Co.; mailing address, 15 Union Ave., Mt. Vernon, N. Y.
BROWN, Harold P. (Apr. 3, '02) Elec. Eng., 120-122 Liberty St., New York City.
BROWN, John T., Jr. (May 26, '10) Superintendent, Duquesne Reduction Co., Pittsburgh, Pa.; res., 5448 Stanton Ave.
BROWN, Dr. John W. (July 31, '07) Pres. and Mgr., The Cleveland Electric Metals Co., Forest City Bank Bldg., Cleveland, Ohio.
BROWN, O. W. (Apr. 3, '02) Associate Prof. in Chem., Indiana Univ., Bloomington, Ind.; res., 2943 Park Ave., Indianapolis, Ind.
BROWN, Richard P. (Aug. 25, '16) Pres., The Brown Instrument Co., Wayne and Windrim Avenues, Philadelphia, Pa.
BROWN, W. G., B.S., Ph.D. (Apr. 3, '02) Prof. of Chem., Univ. of Missouri, Columbia, Mo.
BROWNE, David H. (Apr. 3, '02) Metallurgist, International Nickel Co., 43 Exchange Place, New York City.
BROWNE, deCourcy B. (Apr. 26, '13) Met. Eng., Goldschmidt Thermit Co., 90 West St., New York City.
BROWNE, Prof. Wm. Hand, Jr. (Apr. 3, '02) North Carolina College of Agriculture and Mechanic Arts, West Raleigh, N. C.
BROWNLEE, Harold J. (Dec. 31, '15) Redmand Chem. Products Co., 636 W. 22d St., Chicago, Ill.
BRYAN, John K. (Aug. 22, '13) Gen. Foreman, Raritan Copper Works, Perth Amboy, N. J.; res. 151 Water St.
BRYN, Knud (Nov. 24. '11) Director, Kristiania, Norway.
BRYSON, T. A. (Oct. 22, '15) Eng., Tolhurst Steel Co., Troy, N. Y.; mailing address, 2228 15th St.
BUCH, N. W. (Nov. 6, '13) 2507 E. Cumberland St., Philadelphia, Pa.
BUCHANAN, Leonard B. (Apr. 3, '02) Head of Chemical and Industrial Dept., Stone & Webster, 147 Milk St., Boston, Mass.
BUCHERER, Prof. Dr. Alfred H. (May 27, '11) Professor of Physics, Bonn University, Bonn, Germany.
BUCK, C. A. (May 29, '09) Vice-President, Bethlehem Steel Co., South Bethlehem, Pa.
BUCK, H. W. (May 7, '04) 49 Wall St., New York City.

BUCKIE, Robert H. (Sept. 25, '09) c/o New York & Penna. Co., Johnsonburg, Pa.
BULLOCK, Arthur R. (Apr. 24, '14) Electrical Eng.,11913 Lake Ave., Lakewood, Cleveland, Ohio.
BUMGARDNER, J. W. (Aug. 25, '16) Metallurgist, and Supt. Chill Roll Dept., Wheeling Mold and Foundry Co., Wheeling, W. Va.; mailing address, 4 19th St., Warwood, W. Va.
BURDICK, E. C. (Oct. 21, '16) Chemist, Dow Chem. Co., Midland, Mich.
BURGER, Dr. Alfred (Aug. 26, '10) 68 Bay View Ave., New Brighton, New York.
BURGESS, C. F. (Apr. 3, '02) President, C. F. Burgess Labs., 625 Williamson St., Madison, Wis.
BURMAN, Birger F. (Dec. 31, '14) 1717 N. 53d St., Philadelphia, Pa.
BURNS, Willis T. (Nov. 6, '03) Supt., Electrolytic Refinery, Boston and Mont. Cons. Cop. S. and Min. Co., Great Falls, Mont.
BURT-GERRANS, J. T. (Jan. 27, '12) Lecturer in Electrochemistry, University of Toronto, Toronto, Canada; res., 46 Dewson St.
BURWELL, Arthur W. (Nov. 5, '04) Rexford, Lincoln Co., Montana.
BUTCHER, J. C. (Sept. 27, '16) Prop. J. C. Butcher Co., Hood River, Oregon.
BUTTERS, Chas. (July 1, '05) 6272 Chabot Road, Oakland, Cal.
BUTTFIELD, W. J. (Oct. 23. '14) Pres., Vulcan Detinning Co., Sewaren, N. J.
BUTTS, Allison (Dec. 31, '14) Asst. Editor, Mineral Industry, Box 89, So. Bethlehem, Pa.
CALDER, A. R. (May 26, '10) Met., Bethlehem Steel Co., Steelton, Pa.; mailing address, 2200 Bellevue Road, Harrisburg, Pa.
CALHANE, D. F. (June 1, '15) Prof. Electro-Chemistry, Worcester Polytechnic Inst., Worcester, Mass.
CALLAHAN, Joseph F. (Sept. 20, '11) Chemist, Int. Acheson Graphite Co., Niagara Falls, N. Y.; res., 522 Jefferson Ave.
CALLEN, A. S. (Apr. 24, '14) Res. Chemist, Wedge Mechanical Furnace, Philadelphia; mailing address, 3510 N. 16th St.
CAMERON, Frank K., Ph.D. (Oct. 7, '05) Consult. Chemist & Chem. Eng., 3207 19th St., N. W., Washington, D. C.
CAMERON, Walter S. (Apr. 3, '02) 239 W. 136th St., New York City.
CAMPBELL, Donald F. (Feb. 27, '09) Electrometallurgist, 17 Victoria St., London, S. W., England.
CANBY, Robt. C. (July 24, '14) Consulting Metallurgist, 334 So. Main St., Wallingford, Conn.
CANET, B. Charles (Aug. 26, '10) 121 Maiden Lane, New York City.
CANTLEY, Thomas (Mar. 27, '09) Gen. Manager, Nova Scotia Steel & Coal Co., Ltd., New Glasgow, Nova Scotia, Canada.
CARHART, Prof. H. S. (Apr. 3, '02) Prof. Emeritus of Physics, Univ. of Mich., Ann Arbor, Mich.; mailing address, 277 N. El Molino Ave., Pasadena, Cal.
CARLSON, Birger (Nov. 5, '04) Chemist, Electrochem. Works of Stockholm Superfosfat Aktiebolag of Stockholm, Sweden; res., Mansbo, Avesta, Sweden.
CARNEGIE, Ebenezer (Aug. 28, '14) Pres. and Gen. Mgr., The Electric Steel and Metals Co., Ltd., Welland, Ont., Canada.
CARRIER, C. F., Jr. (Mar. 5, '05) 1567-B Lee St., Charleston, W. Va.
CARRIER, S. C. (Sept. 27, '16) Salesman, Westinghouse Elec. & M. Co., 761 Ocean Ave., Brooklyn, N. Y.
CARRIER, W. H. (Dec. 31, '15) Pres. and Chief Eng., Carrier Eng. Co.; mailing address, 603 Mutual Life Bldg., Buffalo, N. Y.
CARSE, David B. (Mar. 4, '05) President, David B. Carse & Co., 165 Broadway, New York City.
CARTER, F. E. (Aug. 25, '16) Physical Metallurgist, Baker & Co., Inc., c/o Baker Platinum Works, Newark, N. J.
CARVETH, H. R., Ph. D. (Apr. 3, '02) Works Mgr., Niagara Electrochemical Co., Niagara Falls, N. Y.; res., 118 Buffalo Ave.
CARY, Charles R. (May 29, '09) Engineering Salesman, The Leeds & Northrup Co., 4901 Stenton Ave., Philadelphia, Pa.
CASE, Theodore W. (Dec. 30, '16) Auburn, N. Y.
CASE, Willard E. (Oct. 2, '02) Metropolitan Club, 5th Ave. and 60th St., New York City.
CASE, Willis W., Jr. (Nov. 27, '09) Denver Athletic Club, Denver, Colo.
CASSELBERRY, Harry (June 29, '07) 2218 4th Ave., Altoona, Pa.
CASTLE, S. N. (Jan. 27, '12) Davenport Neck, New Rochelle, N. Y.
CHALAS, Adolphe (May 29, '09) care of Chalas & Sons, Finsbury Pavement House, Finsbury Pavement, London, E. C., England.
CHANDLER, Dr. C. F. (Jan. 8, '03) Prof. of Chem., Columbia Univ., New York.
CHANEY, N. K. (Mar. 27, '14) Res. Chemist, The National Carbon Co., Cleveland, Ohio; mailing address, 1614 Wyandotte Ave., Lakewood, Ohio.
CHAPIN, Dr. H. C. (Apr. 22, '15) Research Chemist, Nat. Carbon Co.,; mailing address, 1276 W. 112 St., Cleveland, Ohio.
CHEDSEY, Wm. R. (Apr. 24, '09) Min. & Met. Eng., 1414 Gaylord St., Denver, Colo.
CHERRY, Louis B. (Dec. 31, '15) Electrochemist and Elec. Eng., 501 Knickerbocker, Kansas City, Mo.
CHIARAVIGLIO, Dino (Apr. 3, '02) Via Treviso 7, Rome, Italy.
CHILD, Ernest (Oct. 22, '15) 120 Liberty St., New York City.

CHILD, Hugh A. (Aug. 25, '16) Mgr. and Supt., Bayard Chem. Co., Woodbridge, N. J.
CHILDS, D. H. (Apr. 3, '02) Head of Science Dept., Technical High School, Buffalo, N. Y.; mailing address, 261 Huntington Ave.
CHILLAS, Richard B., Jr. (May 5, '10) Chemical Engr., National Carbon Co., Cleveland, Ohio; res., 1276 W. 112th St.
CITO, C. C. (Sept. 26, '08) Consulting Engineer, Director and Gen Mgr., of the Mines de Monte Zippiri Sardaigne, 10 Rue Henri Marichal, Brussels, Belgium.
CLAMER, G. H., (Apr. 3, '02) Ajax Metal Co., Frankford Ave. and Richmond St., Philadelphia, Pa.
CLAPP, E. H. (Sept. 4, '03) Vice-Pres., Penobscot Chem. Fibre Co., 49 Federal St., res., 490 Beacon St., Boston, Mass.
CLAPP, Joseph F. (Nov. 27, '09) Metallurgist, Rare Metals Corporation, Los Angeles, Cal.; res., 3118 Humboldt St., Los Angeles, Cal.
CLARK, Friend E., Ph.D. (Apr. 3, '02) The Dept. of Chem., West Virginia Univ., Morgantown, W. Va.
CLARK, Walter G. (Sept. 28, '07) Pres. Parker-Clark Electric Co., 135 Broadway, New York City.
CLARK, Wm. J. (Apr. 3, '02) Gen. Mgr. Foreign Dept., Gen. Elec. Co., 44 Broad St., New York City.
CLARK, Wm. W. (May 27, '11) Gen. Mgr., Noble Electric Steel Co., Heroult, Cal.
CLARKE, Eben B. (June 25, '09) General Manager, Firth-Sterling Steel Co, McKeesport, Pa.
CLEAVES, Dr. Margaret A. (Mar. 5, '04) Physician in active practice, c/o T. E. Schulte, 132 E. 23d St., New York City.
CLEMENTS, Frank O. (Apr. 29, '11) Chemist, The National Cash Register Co., Dayton, Ohio.
CLEVENGER, G. H. (Aug. 27, '09) Consulting Engineer, Butters Salvador Mines; mailing address, 381 Hawthorne Ave., Palo Alto, Cal.
CLYMER, W. R. (May 30, '08) Factory Mgr., National Carbon Co.; mailing address, 13985 Lake Ave., Cleveland, Ohio.
COATES, Jesse (May 29, '09) 40 Ocean Ave., Lynn, Mass.
COFFIN, F. P. (May 25, '12) Electrical Engineer, General Electric Co., Schenectady, N. Y.; res., 69 Bedford Road.
COGGESHALL, G. W. (Apr. 3, '02) Chem. Eng., The Inst. of Industrial Res., Washington, D. C.; mailing address, 2229 California St.
COHO, H. B. (Apr. 3, '02) United Lead Co., 111 Broadway, New York City.
COHOE, W. P. (Oct. 28, '09) Consulting Chemist, 50 E. 41st St., New York City.
COLBY, Ed. A. (Apr. 3, '02) Supt., Baker Platinum Works, Newark, N. J.
COLCORD, Frank F. (Oct. 7, '05) c/o U. S. Metal Ref. Co., 120 Broadway, New York City.
COLE, Chas. S. (Dec. 31, '15) Sec'y and Treas., Columbia Steel Co., 820 Penobscot Bldg., San Francisco, Cal.
COLE, Edward R. (June 25, '09) Assistant Superintendent, International Acheson Graphite Co., Niagara Falls, N. Y.
COLLETT, Emil (Nov. 24, '11) Solligaten 7, Kristiana, Norway.
COLLETT, Ove (Feb. 23, '12) Met. Engr., Gronnegate 6, Kristiania, Norway.
COLLINS, Fred L. (Oct. 29, '08) Elec. Engr., Dominion Iron and Steel Co., 160 Whitney Ave., Sydney, Cape Breton, Nova Scotia, Canada.
COLVOCORESSES, Geo. M. (Dec. 31, '09) Gen. Mgr., Consolidated Arizona Smelting Co., Humboldt, Arizona.
COMEY, Arthur M. (Apr. 29, '11) Director, Eastern Laboratory, E. I. du Pont de Nemours Powder Co., Chester, Pa.; res., 424 E. 13th St.
COMSTOCK, Chas. W. (June 27, '13) Consult. Eng., 1235 First Nat. Bank Bldg., Denver, Colo.
COMSTOCK, D. F. (Mar. 27, '14) Eng. and Assoc. Prof. of Physics, Mass. Inst. of Technology, Cambridge, Mass.
CONKLIN, E. B. (Oct. 21, '16) Eng. Semet Solvay Co., 236 W. Borden Ave., Syracuse, N. Y.
CONNELL, H. R. (May 26, '10) Allegheny Steel Co., Brackenridge, Pa.; res., Tarentum, Pa.
CONNELL, Wm. H. (May 27, '11) Treasurer, American Bridge Co., Frick Bldg., Pittsburgh, Pa.
CONVERSE, Vernon G. (Oct. 29, '08) General Mgr. and Chief Engineer, The Ontario Power Co.; P. O. Box 496, Niagara Falls, N. Y.
CONVERSE, W. A. (Nov. 27, '09) Secretary and Chemical Director, Dearborn Drug and Chemical Co., Chicago, Ill.; mailing address, 4320 Greenwood Ave.
COOK, Edw. B. (May 5, '10) 1568 E. 108 St., Cleveland, Ohio.
COOLEY, E. K. (Apr. 26, '16) Prop. San Francisco Galvanizing Wks., 1176-1180 Harrison St., San Francisco, Cal.
COOLIDGE, Wm. D. (June 27, '13) Asst. Director, Res. Lab., Gen. Elec. Co., Schenectady, N. Y.
COOPER, H. C. (Nov. 26, '15) Prof. of Physical Chem., Syracuse University, Syracuse, N. Y.
COOPER, K. F. (Feb. 27, '09) Vice-Pres., American Cyanamid Co., 200 Fifth Ave., New York City.
COPE, F. T. (Jan. 25, '13) Engineer, c/o Electric Furnace Co., Alliance, Ohio.

COPEMAN, L. G. (Aug. 25, '16) Designing Eng., Copeman Electric Stove Co., 1715 Detroit St., Flint, Mich.
CORBIN, J. Ross (May 26, '10) Boyerstown, Pa.
CORNING, Christopher R. (July 21, '11) 36 Wall St., New York City; res., Tuxedo Park, N. Y.
CORNTHWAITE, Hayden (Sept. 25, '09) c/o 2 The Avenue, Brimsdown, Middlesex, England.
CORSE, Wm. M. (May 5, '10) Mgr. Bronze Dept., The Titanium Alloy Mfg. Co., Niagara Falls, N. Y.; res., 106 Morris Ave., Buffalo, N. Y.
COTTRELL, F. G. (Dec. 28, '12) Chief Metallurgist, U. S. Bureau of Mines, Washington, D. C.
COWAN, Wm. A. (May 5, '10) Assistant Chemist, Research Laboratories, National Lead Co., 129 York St., Brooklyn, N. Y.
COWLES, Alfred H. (Apr. 3, '02) The Elec. Smelt. and Aluminum Co., P. O. Box 84, Sewaren, N. J.
COWLES, Harry D. (Dec. 28, '12) Res. Chemist, 166 N. 17 St., East Orange, N. J.
COWPER-COLES, S. (Oct. 10, '03) 1 and 2 Old Pye St., Westminster, London, S. W., England; mailing address, "The Cottage," French St., Sunbury on Thames.
COWPERTHWAIT, Arthur D. (Aug. 25, '16) Chem. Eng., The Edmunds & Jones Corp., Detroit, Mich.
COX, G. E. (Apr. 3, '02) Works Mgr., American Cyanamid Co., Niagara Falls, N. Y.
COX, Harold N. (Oct. 21, '16) Supt. Enamel Div. and Chief Chemist, c/o Lalance & Grosjean Mfg. Co., Woodhaven, N. Y.
COX, Samuel F. (June 1, '15) c/o Pittsburgh Plate Glass Co., Creighton, Pa.
CRABTREE, Prof. Fred. (May 29, '09) Prof. of Metallurgy and Mining, Carnegie Technical Schools, Pittsburgh, Pa.; mailing address, 6214 Stewart St.
CRAFTS, Walter N. (Aug. 25, '11) President, Crucible Steel Forge Co., Cleveland, Ohio; res., Oberlin, Ohio.
CRANE, F. D. (Oct. 29, '08) Research Chemist, Synfleur Sci. Labs., Monticello, N. Y.; mailing address, 28 Hillside Ave., Montclair, N. J.
CRANSTON, John (Oct. 21, '16) Chemist, Penna. Salt Mfg. Co.; mailing address, Box 101, Wyandotte, Mich.
CREIGHTON, Elmer E. F. (Apr. 3, '02) Consult. Eng., General Electric Co., Schenectady, N. Y.; mailing address, 27 Wendell Ave.
CREIGHTON, H. J. (June 2, '16) Asst. Prof. of Chemistry, Swarthmore College, Swarthmore, Pa.
CRIDER, J. S. (May 9, '03) Secretary, National Carbon Co., Cleveland, Ohio.
CRIM, L. P. (Jan. 29, '09) Engineer, care of Pacific Tel. & Tel. Co., 731 Henry Bldg., Seattle, Washington.
CROCKER, Jas. R. (Feb. 25, '11) Chief Eng., Permutit Co., 30 E. 42d St., New York City; res., 202 W. 79th St., New York City.
CROSBY, E. L. (Dec. 28, '12) Sales Engr., 18 Washington Blvd., Detroit, Mich.
CUMMINGS, William J., C.E. (Dec. 31, '09) Chief Engineer, E. I. du Pont Powder Co., Haskell, N. J.
CUNNINGHAM, Frederick Wm. (Dec. 29, '11) Advisory Consultant, c/o Powdered Coal Eng. and Equipment Co., 2401 Washington Blvd., Chicago, Ill.; mailing address, 821 Lake St., Oak Park, Ill.
CURFMAN, F. G. (July 25, '15) 519 International Bldg., St. Louis, Mo.
CURTISS, John L. (Mar. 26, '15) Local Eng., Buffalo, N. Y.; mailing address, Gen. Elec. Co., 10th floor, Gen. Elec. Bldg., Buffalo, N. Y.
CUSHING, H. M. (May 27, '14) Engineer, Buffalo General Elec. Co., Buffalo, N. Y.; mailing address, R. D. No. 1, Williamsville, N. Y.
CUSHMAN, A. S. (June 1, '07) Director, The Inst. of Industrial Research, 19th and B Sts., N. W., Washington, D. C.; res., 1751 N Street.
CUTTS, V. O. (June 27, '13) Electrometallurgist, Town Hall Chambers, 87 Fargate, Sheffield, England.
CZARNECHI, F. C. (July 25, '15) c/o Penna. Utilities Co., Easton, Pa.
DABOLT, Newton E. (Apr. 26, '13) Chemist, Room 740, 200 5th Ave., New York City; mailing address, 304 So. 5th Ave., Mt. Vernon, N. Y.
DAFT, Leo (Mar. 27, '09) Consulting Electrical Engineer, Rutherford, N. J.
DAINES, W. P. (Sept. 27, '16) Chief Chemist, Columbus Iron & Steel Co., Columbus, Ohio.
DALBEY, G. E. (Sept. 27, '16) Supt. of Electrolytic Zinc Plant and Red. Co.; mailing address, 4234 Wirt St., Omaha, Neb.
DALTON, A. C. (Mar. 24, '16) Met., Nova Scotia Steel and Coal Co., P. O. Box 8, New Glasgow, Nova Scotia.
DAPPLES, Alfred (Oct. 29, '08) Directeur, Societe Fabbricaziane del Aluminio, Bussi-Afficienne, Aguila, Italy.
DARRAH, Wm. A. (Aug. 25, '16) Chief Eng., Ohio Brass Co., Mansfield, Ohio.
DAVIDSON, T. R. (Sept. 27, '16) Director, The Thos. Davidson Mfg. Co., Ltd., P. O. Box 700, Montreal, Canada.
DAVIS, D. L. (Aug. 7, '02) Supt. The Salem Elec. L. and P. Co.; res., 299 Lincoln Ave., Salem, Ohio.
DAVIS, F. W. (May 24, '13) Fuel Chemist, Alan Wood Iron and Steel Co., Conshohocken, Pa.

DAVIS, Hugh N. (Sept. 27, '16) Asst. Met., Keokuk Electro-Metals Co., 124 North 4th St., Keokuk, Iowa.
DAVISON, A. W. (Mar. 24, '16) Charge of Phy. and Applied Electrochem., Dept. of Chemistry, Univ. of Cincinnati, Ohio.
DEACON, Ralph W. (May 5, '10) Supt., United States Metals Ref. Co., Chrome, New Jersey.
DEAGLE, L. M. (Oct. 21, '16) Electrician, Cataract Elec. Co. Ltd., Orangeville, Ont., Canada.
DE BEERS, F. M. (May 29, '09) Pres. & Gen. Mgr., Swenson Evaporator Co., 945 Monadnock Bldg., Chicago, Ill.
DEEDS, E. A. (Nov. 6, '02) Asst. Gen. Mgr., National Cash Register Co., 319 Central Ave., Dayton, Ohio.
DE FOREST, C. M. (Dec. 31, '14) Asst. Mgr., Sowers Mfg. Co., Buffalo, N. Y.; mailing address, 152 Clinton St., Tonawanda, N. Y.
DE GEOFROY, Antoine (Jan. 25, '13) 12 rue du Bouquet, de Long Champs, Paris, France.
DE JOANNIS, Harry (May 22, '14) Managing Editor, "Brass World & Platers' Guide," Bridgeport, Conn.
DE MEDEIROS, Trajano (Jan. 29, '10) Rua de Sao Jose, No. 76, Rio De Janeiro, Brazil.
DEMOREST, D. J. (Aug. 25, '16) Prof. of Met., Dept. of Metallurgy, Ohio State Univ., Columbus, Ohio.
DE NEUFVILLE, Dr. R. (Feb, 5, '03) Junghofstrasse 14, Frankfort a/M, Germany.
DEPPE, Wm. P. (Dec. 30, '16) Manufacturer, 127 Duane St., New York City.
DESHLER, Geo. O. (Oct. 24, '13) Supt., Mines Operating Co., Butte, Mont.
DE SOUZA, Edgard (Dec. 31, '09) Chief Electrical Engineer, The S. Paulo Tramway Light and Power Co., Ltd., S. Paulo, Brazil; mailing address, Caixa 162.
DETWILER, J. G. (Dec. 30, '16) Chemist, Res. Lab., The Texas Co., Port Arthur, Texas.
DEVEREUX, Washington (Jan. 6, '06) Inspector, Phila. Fire Underwriters' Association, 1625 N. 29th St., Philadelphia, Pa.
DEVERS, Philip K., Jr. (Jan. 27, '12) Research Engineer, Res. Lab., The General Electric Co., West Lynn, Mass,; res., 30 Hanover St., Lynn Mass.
DEWEY, Bradley (Jan. 28, '11) Director, Research Laboratory, Am. Sheet & Tin Plate Co., 210 Semple St., Oakland, Pittsburgh, Pa.
DEWEY, Edwin S. (Dec. 26, '13) 162 Elmwood Ave., Newark, N. J.
DEWEY, F. P. (Apr. 2, '04) Assayer, Bureau of Mines, 832 Varnum St., N. W., Washington, D. C.
DIACK, Archibald W. (July 21, '11) Diack & Smith, 49 West Larned St., Detroit, Mich.
DIAZ-OSSA, Prof. Belisario (June 25, '09) Prof. of Technology, University of Chile, Casilla No. 962, Santiago, Chile, South America.
DITTMAR, Carl (June 2, '16) Sales Mgr., Electroplating Dept., Roessler & Hasslacher Chem. Co., 2212 Union Central Bldg., Cincinnati, Ohio.
DIXON, Jos. L. (Oct. 23, '14) Engineer, John A. Crowles Co., New York City; mailing address, 120 Liberty St.
DODGE, Col. David C. (Apr. 29, '11) 1654 Broadway, Denver, Colo.
DOERFLINGER, Wm. F. (July 3, '02) Perry Austin Mfg. Co., Grasmere, Staten Island, New York City.
DOERSCHUK, Victor C. (Apr. 29, '11) Massena, N. Y
DONY-HENAULT, Prof. O. (Feb. 27, '14) 40, Avenue de Bertaimont, Al Ecole des Mines, Mons, Belgium.
DOOLITTLE, C. E. (May 9, '03) Consulting Hyd. & Elec. Engr., V.-Pres. & Gen Mgr., The Roaring Fork Elec. Light and Power Co., Aspen Col.
DOREMUS, Dr. Chas. A. (Apr. 3, '02) 55 W. 53d St., New York City.
D'ORNELLAS, Thomas V. (Nov. 21, '08) El. Eng., Peruvian Govt., Calle de Lima 15, Chorrillos, Lima, Peru, S. A.
DORR, J. V. N. (Nov. 28, '13) Pres., The Dorr Co., Cooper Bldg., Denver, Colo.; mailing address, 17 Battery Place, New York City.
DORSEY, H. G. (Oct. 3, '12) Gloucester, Mass.
DOTY, Ernest L. (Sept. 26, '08) Dist. Eng., Westinghouse El. & Mfg. Co., 6 and 8 Lock St., Buffalo, N. Y.; res., 546 Potomac Ave.
DOUBLEDAY, Ralph S. (Aug. 25, '16) Chief Chemist, Marden Orth & Hastings Co., Milford, N. J.
DOUGHERTY, John W. (Feb. 27, '09) President, Pittsburgh Crucible Steel Co., Pittsburgh, Pa.
DOUGLAS, J. (Nov. 27, '09) The Phelps-Dodge Co., 99 John St., New York City.
DOW, Herbert H. (Apr. 3, '02) Midland, Mich.
DOWNES, Arthur C. (July 30, '09) Chemist, National Carbon Co., Fostoria, Ohio.
DRAEGER, A. Bernhard (Nov. 26, '07) Draeger Werke, Lubeck, Germany.
DREFAHL, L. C. (Oct. 22, '15) Res. Chem., Grasselli Chemical Co., 3132 W. 15th St., Cleveland, Ohio.
DREYFUS, Dr. Wm. (Dec. 4, '02) Chem. and Mgr., West Disinfecting Co., 57 E. 96th St., New York City.
DRIVER, Wilbur B. (Aug. 25, '16) Member Board of Directors, Driver-Harris Wire Co., Newark, N. J.

DROBEGG, Dr. Gustave (Jan. 8, '03) Sup't Plant D, Butterworth-Judson Corp., Newark, N. J.
DRYER, Ervin (Sept. 4, '03) Peoples Gas Bldg., Chicago, Ill.
DUDLEY, Boyd, Jr. (Nov. 28, '13) Asst. Prof. of Metallurgy, Penna. State College, State College, Pa.
DuFAUR, J. B. (June 1, '07) Burra Copper Mine, Kooringa, So. Australia.
DUNCAN, Thos. (Nov. 6, '03) Vice-Pres, and Gen. Mgr., Duncan Elec. Mfg. Co., 317 S. 6th St., LaFayette, Ind.
DUNLAP, Orrin E. (July 31, '08) Sec'y, Int. Acheson Graphite Co., Niagara Falls, N. Y.
DUNN, J. J. (Feb. 25, '11) General Supt. and Chief Engr., Shelby Steel Tube Co., Elwood City, Pa.
DUNNINGTON, Prof. F. P. (Apr. 6, '11) Professor of Analytical and Industrial Chemistry, University of Virginia, University, Va.
DU PONT, Irenee (Apr. 24, '09) V. Pres., E. I. du Pont de Nemours Powder Co., Wilmington, Del.
DU PONT, Pierre S. (Jan. 29, '09) Treas., E. I. du Pont de Nemours Powder Co., Wilmington, Del.
DURANT, W. Clark (Oct. 21, '16) Sales Mgr., New England Power Co., Worcester, Mass.
DUSCHAK, L. H. (June 25, '09) Chem. Eng., U. S. Bureau of Mines, Mining Bldg., Berkeley, Cal.; mailing address, 1301 Tamalpais St.
DUURLOO, F. (Oct. 21, '16) Asst. Sec'y, W. R. Grace & Co., N. Y.; mailing address, 131 Caryl Ave., Yonkers, N. Y.
DWIGHT, Arthur S. (Feb. 26, '10) Consulting, Mining and Met. Eng., 29 Broadway, New York City.
DYRSSEN, W. (Jan. 23, '14) Metallurgist, 271 Hicks St., Brooklyn, N. Y.
EAGLE, Henry Y. (Nov. 30, '12) Box 947, Great Falls, Mont.
EASTMAN, Herbert C. (May 5, '10) Manager and Owner, The Ontario-Colorado Gold Mining Co., and The Colo.-Wyoming Power & Irrigation Co., 719-720 Equitable Bldg., Denver, Col.
EASTMAN, H. M. (Feb. 25, '16) Supt., The National Radium Inst.; mailing address, 457 South Elati St., Denver, Colo.
ECKER, Howard, Jr. (Oct. 21, '16) 3115 Woodburn Ave., Cincinnati, Ohio.
EDE, Joseph A. (Oct. 29, '10) Consulting Mining Eng., Illinois Zinc Co., La Salle, Ill.
EDISON, Thos. A. (Apr. 4, '03) Orange, N. J.
EDMANDS, I. R. (Aug. 7, '02) Consult. Eng., Union Carbide Co., Niagara Falls, N. Y.; mailing address, 167 Buffalo Ave.
EDSTROM, J. Sigfrid (Nov. 5, '04) Managing Dir., General Electric Co. of Sweden, Vesteras, Sweden.
EGLIN, Wm. C. L. (July 1, '04) Elec. Eng., 1000 Chestnut St., Philadelphia, Pa.
EIMER, A. (Dec. 4, '02) Eimer & Amend, 205-211 Third Ave., New York City.
EKELEY, John B. (Feb. 21, '13) Prof. of Chemistry, Univ. of Colo., Boulder, Colo.; res., 525 Highland Ave.
ELDRIDGE, Samuel E. (Sept. 27, '15) Eng., Columbus Iron and Steel Co., Columbus, Ohio.
ELLIOTT, Geo. K. (Dec. 30, '16) Chief Chem. and Met., The Lunkenheimer Co., Cincinnati, Ohio.
ELLIS, Carleton (Jan. 23, '14) Industrial Res. Chemist, 92 Greenwood Ave., Montclair, N. J.
ELY, Theodore N. (Apr. 3, '02) Bryn Mawr, Pa.
EMANUEL, Louis V. (Oct. 17, '07) care of River Smelt. & Ref. Co., Florence, Colo.
EMERSON, Harrington (Feb. 25, '11) President, The Emerson Co., 30 Church St., New York City.
EMERY, A. L. (Apr. 3, '02) Smith, Emery & Co., Chem. and Met. Engs., Howard and Hawthorne Sts., San Francisco, Cal.
EMERY, W. L. (Sept. 26, '08) Foreman of Meter Dept., Utah Lt. & Ry. Co.; mailing address, 43 N. 7th West St., Salt Lake City, Utah.
ENGELHARD, Chas. (May 29, '09) President, American Platinum Works, Newark, N. J.; mailing address, Hudson Terminal Bldg., 30 Church St., New York City.
ENGELHARDT, Victor (Dec. 4, '02) Siemens & Halske Co.; res., Charlottenburg, Oranienstrasse 18, Germany.
ERHART, W. H. (Dec. 27, '07) 11 Bartlett St., Brooklyn, N. Y.
ERICSON, Eric J. (Oct. 24, '13) Chief Chemist, Edgar Zinc Co., Cherryvale, Kansas.
EURICH, E. F. (Nov. 27, '09) Mining and Metallurgical Engineer, 15 William St., New York City; res., Montclair, N. J.
EUSTIS, Augustus H. (Dec. 31, '09) Mining Engineer, 131 State St., Boston, Mass.
EVANS, H. S. (Apr. 3, '02) Prof. Elec. Eng., Univ. of Col., Boulder, Col.
EVERETTE, Dr. Willis E. (July 30, '09) Consulting Chemical and Mining Engineer, Tacoma, Wash.
FALTER, Philip H. (Aug. 25, '11) Gen. Mgr., Shawinigan Electro Products Co., Baltimore, Md.; mailing address, 1606 Lexington St. Bldg.
FARNHAM, Frederick F. (May 26, '10) Chemist, c/o National Metal Molding Co., Ambridge, Penna.

FARROW, Percival R. (June 30, '16) Power Station Supt., Kaministiquia Power Co., Ltd., Kakabeka Falls, Ontario, Canada.
FARUP, Dr. P. (Jan. 28, '16) Tekniske Hoiskole, Trondhjem, Norway.
FATTINGER, Dr. Franz (Mar. 23, '12) Treibach, Carinthia, Austria.
FAWCETT, Lewis H. (May 25, '12) Chemist, American Vanadium Co., Crafton, Penna.
FAWCETT, Percy (Sept. 25, '09) Director, Thomas Firth & Sons, Ltd., Sheffield. England.
FEHNEL, J. Wm. (June 26, '14) 703 N. Main St., Bethlehem, Pa.
FERNBERGER, H. M. (Jan. 8, '04) 66 Millington Ave., Newark, N. J.
FERNEKES, Gustave (Oct. 22. '15) Chemist, The Am. Conduit Mfg. Co., Oakmont, Pa.
FERRY, Chas. (June 21, '11) Metallurgist, Bridgeport Brass Co., Bridgeport, Conn.
FICHTER-BERNOULLI, Prof. Dr. F. (Nov. 26, '07) 35 Neubadstrasse, Basel, Switzerland.
FINCKH, Dr. Carl (Apr. 24, '14) Asst. Director, Deutsche Gasglühlicht Aktiengesellschaft (Auergesellschaft) Rotherstrasse 8/12, Berlin 0.17, Germany.
FINK, Dr. Colin G. (Nov. 26, '07) Research Chemist, Edison Lamp Works, General Electric Co., Harrison, N. J.; mailing address, 401 Park Ave., East Orange, N. J.
FINNEY, John H. (Oct. 22, '15) Mgr. Southern Office, Aluminum Co. of America, 509 Met. Bank Bldg., Washington, D. C.
FISCHER, Siegfried (Feb. 25, '11) 401 Boston Bldg., Denver, Colo.
FISH, Job, Jr. (Jan. 28, '16) Works Mgr., The Otis Elevator Co.; mailing address, Box 156, Buffalo, N. Y.
FISHER, Henry W. (May 26, '10) Chief Engineer, Standard Underground Cable Co., Perth Amboy, N. J.
FITZGERALD, F. A. J. (Apr. 3, '02) The FitzGerald Laboratories, Inc., Highland and Vermont Aves., Niagara Falls, N. Y.
FITZ GIBBON, R. (Apr. 3, '02) Room 212, 43 Leonard St., New York City.
FLANNERY, Jas. J. (May 26, '10) President, American Vanadium Co., 325 Frick Bldg., Pittsburgh, Pa.
FLEMING, R. (Apr. 3, '02) Chief Engineer, Aetna Explosives Co., Inc., 2 Rector St., Perth Amboy, N. J.; mailing address, 219 Prospect St., So. Orange, N. J.
FLEMING, S. H. (Nov. 26, '10) Research Laboratory, National Carbon Co., Cleveland, Ohio.
FLETCHER, W. E. (Aug. 25, '16) Chem. Director, Atlas Powder Co., Wilmington, Del.
FLIESS. R. A. (Sept. 4, '02) 99 Claremont Ave., New York City.
FLOWERS, Alan E. (Oct. 29, '08) Ohio State University, Electrical Engineering Dept., Columbus, Ohio.
FOERSTERLING, Dr. Hans (Apr. 3, '02) Roessler & Hasslacher Chem. Co., Perth Amboy, N. J.; mailing address, 380 High St.
FOGARTY, John A. (Oct. 21, '16) Asst. Supt., Electrolytic Plant, Burgess Sulphite Fibre Co.; mailing address, 166 Prospect St., Berlin, N. H.
FOLEY, Chas. B. (July 25, '13) 170 Broadway, New York City.
FOOTE, Arthur DeWint (Feb. 27, '09) Superintendent, North Star Mines, Grass Valley, Cal.
FORBES, Geo. S. (May 26, '15) Asst. Prof. of Chem., Harvard University; mailing address, Boylston Hall, Cambridge, Mass.
FORCHHEIMER, Dr. Phil. J. (Dec. 26, '13) Tech. Director, Gesellschaft Eletrometallurgie, 20 Bucherstrasse, Nurnberg, Germany.
FORSSELL, Dr. J. (June 1, '07) 70 A Karlbergsvaegen, Stockholm, Sweden.
FOSTER, Chas. L. (June 30, '16) Sales Mgr., The Electric Furnace Co., 505 Alliance Bank Bldg., Alliance, Ohio.
FOSTER, Oscar R. (Apr. 30, '08) Chemistry Teacher, 203 Eighth Ave., Brooklyn, New York.
FOSTER, Raimond D. (June 1, '15) Treas., care of The Hanson and Van Winkle Co., 269 Oliver St., Newark, N. J.
FOUST, Thos. B. (Jan. 29, '09) Clarksville, Tenn.
FOWLER, R. E. (Nov. 6, '03) Chemist, The National Electrolytic Co., Niagara Falls, N. Y.
FOWLER, Samuel S. (Apr. 3, '02) Min. Eng., P. O. Drawer 1024, Nelson, B. C.
FRALEY, Jos. C. (Apr. 3, '02) Attorney-at-Law, 1815 Land Title Bldg.; res., 1833 Pine St., Philadelphia, Pa.
FRANK, John J. (Dec. 31, '15) Asst. Transformer Eng., General Electric Co.; mailing address, 43 George St., Pittsfield, Mass.
FRANK, Karl G. (Feb. 27, '09) Representative, Siemens & Halske, A. G., West St. Bldg., (90 West St.) Room 408, New York City.
FRANKFORTER, G. B. (April 3, '02) Prof., Univ. of Minnesota, Minneapolis, Minn.
FRANKLIN, Milton W. (May 29, '09) Engineer, Ozonator Dept., Gen. Elec. Co., Bloomfield, N. J.; mailing address, 188 N. Walnut St., East Orange, N. J.
FRANKLIN, Prof. W. S. (Mar. 4, '05) 227 Wall St., Bethlehem, Pa.
FRARY, Francis C. (Aug. 31, '07) Res. Chemist, care of Oldbury Electrochemical Co., Niagara Falls, N. Y.; mailing address, 14 C St.
FREAS, Thos. B. (Oct. 29, '10) Havemeyer Hall, Columbia University, New York City.

FREDERICK, Geo. E., Jr. (Jan. 29, '09) Mgr., Arnold Hoffman Co., P. O. Box 762, New York City.
FREEMAN, Gay N. (July 30, '09) Assayer and Analytical Chemist, Thermopolis, Wyoming.
FREUD, B. B. (Jan. 28, '16) Assoc. Prof. of Chem., Armour Inst. of Tech., Chicago, Ill.
FRICK, Frederick F. (Feb. 26, '15) Res. Eng., Anaconda Copper Min. Co., Anaconda, Mont.
FRICKEY, Royal E. (Sept. 20, '11) Eng., Northern Calif. Power Co., Cons., Redding, Cal.
FRIES, Harold H., Ph.D. (May 1, '06) 92 Reade St., New York City.
FULLER, G. Prescott (Dec. 30, '16) Res. Chemist, National Electrolytic Co., Niagara Falls, N. Y.
FURNESS, Radclyffe (May 29, '09) Engineer in Charge of Research, Midvale Steel Co., Philadelphia, Pa.
GABRIEL, Geo. A. (Apr. 3, '02) 147 Dartmouth St., Portland, Me.
GABY, Frederick A. (Mar. 26, 1915) Chief Eng., Hydro-Elec. Power Commission of Ontario; mailing address, 709 Continental Life Bldg., Toronto, Can.
GAHL, Dr. Rudolf (June 6, '03) c/o Inspiration Cons. Copper Co., Miami, Ariz.
GAILLARD, David St. P. (Aug. 25, '16) Supt. Experimental Plant, American Cyanamid Co., Warners, N. J.; mailing address, 1333 North Ave., Elizabeth, N. J.
GAINES, Richard H. (Oct. 17, '07) Chemist, New York Board of Water Supply, 49 Lafayette St., New York City; res., 35 W. 38th St.
GALL, Henry (Apr. 2, '04) Societe de Electrochimie, 2 Rue Blanche, Paris, France.
GANDILLON, Ami (Jan. 8, '04) Case 6219, Bourg de Four, Geneva, Switzerland.
GANZ, Albert F. (Nov. 21, '08) Consult. Eng., Prof. of Electrical Engineering, Stevens Institute of Technology, Hoboken, N. J.; res., 612 River St.
GARDNER, Henry A. (Oct. 28, '09) The Institute of Industrial Research, Washington, D. C.
GARRATT, Frank (Feb. 21, '13) Latrobe Electric Steel Co., Latrobe, Pa.
GEESON, Arthur (Oct. 21, '16) Supt. Construction and Operation, Molybdenum Products Co., 415 E. 2d St., Tucson, Ariz.
GEGENHEIMER, R. E. (Feb. 27, '14) Chief Chemist, c/o Castner Electrolytic Alkali Co., Niagara Falls, N. Y.
GELSTHARP, Frederick (Aug. 25, '11) Chief Chemist, Pittsburgh Plate Glass Co., Creighton, Pa.; res., Tarentum, Pa.
GEPP, Herbert W. (Aug. 26, '10) General Manager, Amalgamated Zinc (De Bavays) Ltd., Broken Hill, N. S. W., Australia.
GERETY, James Joseph (Oct. 27, '11) Asst. Chemist, S. P. Sadtler & Son, 39 S. 10th St., Philadelphia, Pa.; res., 2650 Coral St.
GERRY, M. H., Jr. (Apr. 3, '02) Gen. Mgr. and Chief Eng., Missouri River Power Co., Helena, Mont.
GERSTLE, John (May 27, '14) 592 W. 3d St., Dayton, Ohio.
GETMAN, F. H. (Apr. 24, '14) Asso. Prof. of Chemistry, Hillside Laboratory, Glenbrook Road, Stamford, Conn.
GEYLER, F. O. (Nov. 25, '15) Secy. and Treas., Niagara Alkali Co., Niagara Falls, N. Y.
GIBBS, Arthur E. (Oct. 2, '02) Mfg. Chemist, c/o Penna. Salt Mfg. Co., Widener Bldg., Philadelphia, Pa.
GIBSON, C. B. (May 26, '10) Sales Dept., Westinghouse Electric & Manufacturing Co., East Pittsburgh, Pa.; mailing address, 1656 Dennistor Ave., Pittsburgh, Pa.
GIERTSEN, Sigurd (Nov. 24, '11) North Western Cyanamide Co., Odda, Norway.
GIFFORD, A. McK. (Feb. 23, '12) Chemical Engr., General Electric Co., Pittsfield, Mass.
GIFFORD, Wm. E. (Apr. 3, '02) Baker & Co., 54 Austin St., Newark, N. J.
GILBERT, Harvey N. (Dec. 31, '15) Res. Chemist, Niagara Electrochemical Co., 442 10th St., Niagara Falls, N. Y.
GILBERTSON, H. A. (Apr. 2, '13) Mgr. and Jr. Member of Firm, Gilbertson & Son, 7561 Pratt Ave., Edison Park, Ill.
GILCHRIST, Peter S. (Apr. 3, '02) Chem. Eng., Charlotte, N. C.
GILES, Irvin K. (May 1, '06) 1531 S. 28th St., Philadelphia, Pa.
GILLETT, Horace W. (Mar. 26, '10) U. S. Bureau of Mines, Morse Hall, Ithaca, N. Y.
GILLIES, P. McP. (Dec. 28, '12) Metallurgist, c/o Hydro Electric Power & Metallurgical Co., Lombard Bldgs., 17 Queen St., Melbourne, Australia.
GILLIGAN, Frank P. (Jan. 23, '14) Treasurer, The Henry Souther Engineering Co., 11 Laurel St., Hartford, Conn.
GIOLITTI, Federico, Ph.D. (Oct. 17, '07) Director General Steel Works, Ansaldo & Co., Cornigliano Ligure, near Genoa, Italy; mailing address, Regio Politecnics, Via dell Ospedale, Torino, Italy.
GLADSON, Prof. W. N. (Apr. 3, '02) Vice-Pres., University of Arkansas; mailing address, 820 W. Maple St., Fayetteville, Ark.
GLASCOCK, B. L. (Feb. 25, '11) c/o Aluminum Co. of America, Maryville, Tenn.
GLAZE, John B. (June 27, '13) Norton Co., Niagara Falls, N. Y.

GLENNIE, Robert D. (June 2, '16) Salesman, General Electric Co., Gluck Bldg., Niagara Falls, N. Y.
GOEPEL, Carl P. (Nov. 4, '05) Patent-counsel, 290 Broadway, New York City.
GOLDSCHMIDT, Dr. Hans (Nov. 6, '03) Chem. Mfr., Essen-Ruhr, Germany.
GOLDSCHMIDT, Heinrich (Oct. 27, '11) Kristiania, Drammensveien 82, Norway.
GOLDSTEIN, Philip (Mar. 26, '15) Prin., The Clerkenwell Plating Works, 155-7-9 Roseberg Ave., London, E. C., England.
GOODALE, Stephen L., A.M., E.M. (May 26, '10) Prof. of Metallurgy, University of Pittsburgh, School of Mines, Pittsburgh, Pa.
GOODRICH, Robt. R. (Jan. 23, '14) Prof. of Met., University of Idaho, Moscow, Idaho.
GOODSPEED, George M. (May 26, '10) Metallurgist, National Wks., National Tube Co., McKeesport, Pa.
GOODWIN, H. M., Ph.D. (Apr. 3, '02) Mass. Inst. of Tech., Cambridge, Mass.
GOODWIN, Joseph H. (Jan. 6, '06) Asst. Supt., National Carbon Co.; mailing address, 1501 McPherson Ave., Fremont, Ohio.
GOODWIN, Dr. Leo Frank (Oct. 29, '08) Chemistry Dept., Queen's University, Kingston, Ontario, Canada.
GOODWIN, W. L., D. Sc. (Apr. 3, '02) Director, School of Mining, Kingston, Ont., Canada.
GORDON, Prof. C. McC. (Apr. 3, '02) Lafayette College, Easton, Pa.
GORDON, Henry A. (Apr. 24, '09) Consulting Engineer, Ben Lomond, Ranfirely Road, Epsom, Auckland, New Zealand.
GOSROW, R. C. (Sept. 27, '16) Apartment 205, Blackstone Apts., Milwaukee, Wis.
GOULD, David F. (Aug. 25, '16) Chem. Eng., General Lead Batteries Co., Chapel St. and Lister Ave., Newark, N. J.
GOVE, Frank S. (June 1, '15) Asst. Chem., American Smelting & Refining Co., Denver, Colo.; mailing address, 378 So. Clarkson St.
GRAVELY, Julian S. (May 25, '12) 66 Elmwood Road, New Haven, Conn.
GRAVES, Walter G. (Mar. 5, '03) Supt., Grasselli Chem. Co.; res., 1950 E. 90th St., Cleveland, Ohio.
GRAY, Jas. H. (Apr. 6, '11) Metallurgical Engr., U. S. Steel Corporation, 71 Broadway, New York City.
GREEN, H. M. (Oct. 23, '14) Supt. of Tankhouse, U. S. Metal Ref. Co., Chrome, N. J.; mailing address, Box 68.
GREEN, S. Stuart (Nov. 24, '16) Met. Chemist, Tivani Elec. Steel Co., P. O. Box 73, Belleville, Ontario, Canada.
GREENLEE, Wm. B. (Nov. 26, '10) Secretary, Greenlee Foundry Co., Chicago. Ill.; res., 726 Kenesaw Terrace.
GREENWOOD, H. D. (Oct. 23, '14) Chief Chemist, c/o U. S. Metals Ref. Co., Chrome, N. J.
GRIFFEN, Henry R. (June 26, '14) 103 Cornell Ave., Swarthmore, Pa.
GRIFFIN, Martin L. (Oct. 1, '04) Manager of Chemical & Electrochemical Depts., The Oxford Paper Co., Rumford, Me.
GRIFFITH, John R. (Feb. 23, '12) Res. Engineer, Norton Co., Niagara Falls, N. Y.; mailing address, 122 First St., Niagara Falls, N. Y.
GROENWALL, Assar (July 29, '10) Managing Director, Aktiebolaget Elektrometall, Ludvika, Sweden.
GROSSMANN, M. A. (Nov. 27, '14) Res. Asst. Metallurgist, American Vanadium Co., Bridgeville, Pa.; mailing address, 235 Custer Ave., Youngstown, Ohio.
GROSVENOR, Dr. Wm. M. (June 1, '07) Chemists Bldg., 50 East 41st St., New York City.
GROWER, Geo. G. (Nov. 5, '04) Coe Brass Mfg. Co.; res., 15 Colony St., Ansonia, Conn.
GRÜBNAU, G. M. (Oct. 21, '16) Wyncote, Montgomery Co., Pa.
GRYMES, Elmer S. (Oct. 23, '14) Asst. Chief Chemist, U. S. Metals Ref. Co., Chrome, N. J.; mailing address, 116 E. 7th Ave., Roselle, N. J.
GUDEMAN, Edward (Feb. 27, '09) Consulting Chemist and Scientific Expert, 903-4 Postal Telegraph Bldg., Chicago, Ill.
GUERBER, Arnold J. (July 31, '08) Chief Chemist, Standard Chemical Co., Canonsburg, Pa.
GUESS, George A. (Aug. 5, '05) Professor of Metallurgy, Toronto University, Toronto, Canada.
GUESS, H. A. (Mar. 27, '14) Managing Director, Mining Dept., American Smelting & Refining Co., 120 Broadway, New York City.
GUITERMAN, Kenneth S. (June 28, '12) Electrochemist, Selby Smelting and Lead Co., 804 Merchants Exchange Bldg., San Francisco, Cal.
GUMAER, P. W. (Jan. 23, '14) Gen. Elec. Co., Pittsfield, Mass.
GUYE, Prof. Phillippe A. (Dec. 4, '02) 3 Chemin Bizot, Florissant, Geneve, Switzerland.
HAANEL, Dr. Eugene (July 31, '07) Director of Mines, Dept. of Mines, Ottawa, Canada.
HABER, Prof. Dr. F. (Nov. 6, '02) Kaiser Wilhelm-Institut für Physikalische Chemie und Elektrochemie, Berlin-Dalem, Faradayweg 4, Germany.
HADFIELD, R. A. (July 6, '06) Manag. Dir., Hadfield Steel Fdy. Co., Ltd., Parkhead House, Sheffield, England.
HALL, Arthur E. (Apr. 29, '11) Gen. Supt., Am. Smelt. & Ref. Co., Omaha, Neb.

HALL, C. A. (July 25, '15) Cresheim Arms, Mt. Airy, Philadelphia, Pa.
HALL, E. L. (Oct. 21, '16) Chief Eng., Portland Gas and Coke Co., 294 Yamhill St., Portland, Oregon.
HALL, Henry M. (Feb. 25, '11) Supt., U. S. Aluminum Co., Massena, N. Y.; P. O. Box 97, Massena, N. Y.
HALL, M. L. (May 24, '13) 555 S. Los Robles Ave., Pasadena, Cal.
HAMANN, A. M. (June 1, '15) E. E., Niagara Electrochemical Co., Niagara Falls, N. Y.; mailing address, 212 Sixth Street.
HAMBLY, Frederick J. (May 27, '11) Chief Chemist, Electric Reduction Co., Ltd., Buckingham, Quebec, Canada.
HAMBUECHEN, Carl (Apr. 3, '02) Sec'y and Asst. Gen. Mgr., American Carbon and Battery Co., East St. Louis, Ill.; mailing address, 4 Pennsylvania Ave., Belleville, Ill.
HAMILTON, E. H. (Oct. 22, '15) Mgr. Smelters and Refineries, The Consolidated Min. & Smelt. Co. of Canada, Ltd., Trail, B. C., Canada.
HAMISTER, Victor C. H. (Apr. 27, '12) 521 N. Henry St., Madison, Wis.
HANCOCK, H. Lipson (Mar. 26, '10) General Manager, The Wallaroo & Moonta Mining & Smelting Co., Ltd., Moonta Mines, South Australia.
HANGER, Samuel R. (Sept. 27, '12) Inspector, Test Dept., Penna. R. R., Altoona, Pa.; mailing address, 1021 Highland Place.
HANSCOM, Wm. W. (May 27 ,'11) Consulting Elec. Engr., 848 Clayton St., San Francisco, Cal.
HANSEN, C. A. (May 6, '05) 183 J St., Salt Lake City, Utah.
HANSON, Hugo H. (May 22, '14) Director of Station A, Mass. Inst. of Technology, School of Chemical Engineering Practice; mailing address, Eastern Mfg. Co., South Brewer, Me.
HARDCASTLE, Yellott F. (Oct. 22, '15) Supt., Pennsylvania Salt Mfg. Co., Wyandotte, Mich.
HARDIE, Chas. G. (Nov. 26, '15) Construction Dept., General Electric Co., 1001 Electrical Bldg., Buffalo, N. Y.
HARPER, H. A. (Dec. 31, '15) Foreman, Tailing Retreatment Plant, c/o Braden Copper Co., Rancagua, Chile.
HARPER, Dr. H. W. (Apr. 3, '02) Univ. of Texas, Austin, Texas; mailing address, 2216 Rio Grande St.
HARPER, John L. (Apr. 6, '07) Chief Eng., Hydraulic Power Co.; res., 148 Buffalo Ave., Niagara Falls, N. Y.
HARRINGTON, Dr. E. I. (Apr. 3, '02) 84 Ashburton Ave, Yonkers, N. Y.
HARRIS, Jonathan W. (Sept. 26, '08) Research Chemist, Western El. Co., 463 West St., New York City.
HARRIS, Joseph W. (Apr. 3, '02) Patent Lawyer, 3105 18th St., N. W., Washington, D. C.
HART, Edw., Ph.D. (Aug. 7, '02) Prof. of Chemical Eng., Lafayette College, Easton, Pa.
HART, L. O. (Nov. 27, '09) Electrical Engineer, Driver Harris Wire Co., Harrison, N. J.; res., 232 Washington St., Hoboken, N. J.
HARTLEY, Robt. H. (Dec. 27, '07) Chemist, Hartley Bldg., Fourth Ave. and Smithfield Sts., Pittsburgh, Pa.
HARTWICK, Frank A. (Oct. 21, '16) Process and Res. Chem., R. B. Davis Co., Hoboken, N. J.; mailing address, 21 Northfield Ave., West Orange, N. J.
HARVEY, Frederic A. (Apr. 22, '15) Solvay Process Co., c/o Laboratory, Syracuse, N. Y.
HASLWANTER, Chas. (Apr. 3, '02) 447 Spruce St., Richmond Hill, L. I., N. Y.
HASSLACHER, Jacob (Nov. 26, '07) Pres., Roessler & Hasslacher Chem. Co., 100 William St.; P. O. Box 1999, New York City.
HATCH, Israel (Oct. 28, '09) Asst. Superintendent, Elgin National Watch Co., Elgin, Ill.
HATZEL, J. C. (Apr. 3, '02) 373 Fourth Ave., New York City.
HAWKINS, Laurence A. (Apr. 27, '12) Electrical Engineer, Research Laboratories, General Electric Co., Schenectady, N. Y.
HAYES, Geo. W. (Mar. 26, '10) c/o Marconi Wireless Tel. Co. of America, Aldene, N. J.
HAYES, Junius J. (Sept. 27, '16) Principal of Kane Co. High School, Kanab, Kane Co., Utah.
HAYNES, Justin H. (Mar. 24, '16) Metallurgical Eng., Vindicator Con. Co., Independence, Colo.
HAYWARD, Robert F. (Jan. 29, '10) General Manager, Western Canada Power Co., Ltd., Vancouver, B. C., Canada.
HEATH, H. E. (Apr. 3, '02) 83 Court St., Newark, N. J.
HEATH, R. F. (Oct. 21, '16) Chem. Eng., White Sulphur Springs, Mont.
HEDIN, Joseph E. (Apr. 22, '15) General Supt., Delaware Mills of the Jessup & Moore Paper Co., P. O. Box 124, Wilmington, Del.
HEDLUND, Marten (Apr. 1, '05) Managing Dir., Gullspangs Elektrokemiska Aktienbolag, Gullspang, Sweden.
HEITMANN, Edward (Sept. 26, '08) Elec. Eng., c/o Canadian Crocker-Wheeler Co., Ltd., Belleview Terrace, St. Catherines, Ont., Canada.
HELFENSTEIN, Dr. Alois (June 21, '11) Consulting Engineer, Bastiengasse 50, Vienna, XVIII, Austria.

HELFRECHT, A. J. (Mar. 24, '16) C. F. Burgess Labs., Madison, Wis.
HEMINGWAY, Frank (Nov. 26, '07) Pres. Hemingway & Co., Inc., No. 6, East Union Ave., Bound Brook, N. J.
HENDERSON, C. T. (Mar. 24, '16) Eng., The Cutler Hammer Mfg. Co., F. O. Box 1564, Milwaukee, Wis.
HENDERSON, Ernest G. (June 1, '15) Vice-Pres., c/o The Canadian Salt Co., Windsor, Ont., Canada.
HENDERSON, John B. (Dec. 26, '13) Government Analyst, Brisbane, Queensland, Australia.
HENDRIE, G. A. (Nov. 27, '14) P. O. Box 36, Elizabeth, N. J.
HENDRY, W. Ferris (Nov. 26, '07) Engineer, 463 West St., New York City.
HENSEN, Emil (May 26, '10) 1200 State Ave., Coraopolis, Pa.
HERAEUS, Dr. phil. Wilhelm, Firm of W. C. Heraeus, Ltd., Hanau, Germany.
HERING, Carl (Apr. 3, '02) D. Sc., Consult. Elec. Eng., 210 S. Thirteenth St., Philadelphia, Pa.
HERRESHOFF, James B., Jr. (May 27, '14) Consult. Eng., 524 Beech St., Richmond Hill, Long Island, N. Y.
HERTY, C. H. (Oct. 22, '15) Editor, The Journal of Industrial & Engineering Chem., 35 East 41st St., New York City.
HERZ, Alfred (Feb. 27, '14) Testing Engineer, Public Service Co. of N. Illinois, Room 1322, 72 W. Adams St., Chicago, Ill.
HERZOG, G. K. (Feb. 27, '09) Star Electric Co., Niagara Falls, N. Y.
HESS, Frederick M. (Nov. 27, '09) President and General Manager, Inyo Telephone Co., Bishop, Cal.
HESS, Henry (Feb. 25, '11) 928 Witherspoon Bldg., Philadelphia, Pa.
HESSOM, B. F., Jr. (May 26, '10) General Inspector, Duquesne Light Co., 435 Sixth Ave., Pittsburgh, Pa.; res., 136 Fifth St., Aspinwall, Pa.
HIBBARD, Henry D. (May 30, '08) Consult. Eng., 144 E. Seventh St., Plainfield, N. J.
HIBBERT, Harold (Apr. 22, '15) Research Chemist, Mellon Institute, Univ. of Pittsburgh, Pittsburgh, Pa.
HICKS, Edwin F. (May 26, '10) Chief Chemist, Victor Talking Machine Co., Camden, N. J.; res., 4837 Fairmount Ave., Philadelphia, Pa.
HIGASHI, Sentaro (Sept. 15, '15) Met. and El. Met. Eng., Ikuno Mine, Tajima, Japan.
HIGGINS, Aldus C. (Sept. 4, '02) Sec'y and Gen. Counsel, Norton Co., Worcester, Mass.
HILDEBRAND, Joel H. (Oct. 1, '12) Chem. Lab., Univ. of Cal., Berkeley, Cal.
HILL, Nicholas S., Jr. (Nov. 27, '09) Consult. Eng., 100 William St., New York City; res., 381 William St., East Orange, N. J.
HILL, Stafford (Jan. 27, '12) Electrician, The St. John Del Rey Gold Mining Co., Villa Nova de Lima, Minas Geraes, Brazil.
HILLIARD, John D. (Sept. 26, '08) Glen Falls, N. Y.
HINCKLEY, A. T. (May 25, '12) Chemist, National Carbon Co.; res., 2 C Street, Niagara Falls, N. Y.
HIORTH, Albert C. F. (Dec. 31, '10) Josefinegade 13, Christiania, Norway.
HIORTH, Frederick V. L. (Dec. 26, '07) Electrochem. Eng., Josefinegade 19, I, Christiania, Norway.
HIRSCH, Alcan (June 29, '07) Consulting Chemical Engineer, 50 E. 41st St., New York City.
HIRSCHLAND, Franz H., Dr. Ing. (Dec. 27, '07) Mgr., Goldschmidt Chem. Co., 60 Wall St., New York City.
HITCHCOCK, Fanny R. M. (May 1, '06) 4038 Walnut St., Philadelphia, Pa.
HITCHCOCK, Prof. Geo. G. (July 1, '04) Claremont, Cal.
HITCHCOCK, Halbert K. (Oct. 2, '02) 5710 Bartlett St., Pittsburgh, Pa.
HITE, B. H. (Apr. 4, '03) W. Va. Exp. Station, Morgantown, W. Va.
HOFFMANN, John (Mar. 26, '15) Supt. of Copper Refinery, Balbach Smelt. & Ref. Co., 193 Smith St., Newark, N. J.
HOFFMANN, Rudolf (Dec. 26, '08) Prof. of Metallurgy, Kgl. Bergakademie, Clausthal, Germany; mailing address, 221 Bergstrasse.
HOGABOOM, Geo. B. (Feb. 25, '11) Electroplater, International Silver Co., Factory "E," Meriden, Conn.; mailing address, 561 Stanley St., New Britain, Conn.
HOGE, J. F. D. (Apr. 6, '11) The Maintenance Co., 417 Canal St., New York City. res., 509 W. 121st St., New York City.
HOLE, Ivar (Nov. 26, '15) Asst. Supt., Evje Smelter, Evje per Kristianssand S, Norway.
HOLLER, H. D. (Nov. 26, '15) Asst. Chemist, Bureau of Standards, Washington, D. C.
HOLMES, Major E. (Oct. 23, '14) Res. Chemist, Nat. Carbon Co.; mailing address, 1441 Alameda Ave., Cleveland, Ohio.
HOLSTEIN, Leon Stuart (Sept. 28, '12) N. J. Zinc Co., Palmerton, Pa.; mailing address, 477 Columbia Ave., Palmerton, Pa.
HOLTON, Fred. A. (Apr. 2, '04) Chemist in Patent Causes, 700 10th St., N. W., Washington, D. C.
HOMMEL, Rudolf P. (June 2, '16) Asst. to the Secretary, American Electrochem. Society, Lehigh University, So. Bethlehem, Pa.

HOOD, B. B. (July 23, '15) Asst. to the Supt., U. S. Metals Refining Co., Chrome, New Jersey.
HOOKER, Albert H. (Feb. 27, '09) Hooker Electrochemical Co., Niagara Falls, N. Y.
HOPKINS, Geo. A. (Feb. 25, '11) Metallurgist, Carnegie Steel Co., Munhall, Pa.; res., 464 Swissvale Ave., Wilkinsburg, Pa.
HORNSEY, John W. (May 5, '10) Consulting Engineer, Summit, N. J.
HORRY, Wm. S. (Feb. 5, '03) Cons. Lake Sup. Power Co., Niagara Falls, N. Y.
HORSCH, Wm. G. (Apr. 26, '13) Graduate Student, Dept. of Chem., Univ. of California, Berkeley, Cal.
HOSFORD, Wm. F. (Oct. 22, '15) Eng. of Methods, Western Electric Co., Hawthorne Works, Chicago, Ill.
HOSKINS, Wm. (Apr. 3, '02) Suite 2009, Harris Trust Bldg., 111 W. Monroe St., Chicago, Ill.
HOUGH, Arthur (May 1, '06) Curtis & Harvey, Ltd., 400 St. James St., Montreal, Canada.
HOWARD, Geo. M. (Apr. 3, '02) 19th St. and Allegheny Ave., Philadelphia, Pa.
HOWARD, Henry (Apr. 3, '02) 36 Amory St., Brookline, Mass.
HOWARD, L. E. (May 29, '09) Metallurgist, Simonds Mfg. Co., Lockport, N. Y.; mailing address, 259 Niagara St.
HOWARD, Prof. S. Francis (Apr. 3, '02) Prof. of Chem., Norwich Univ., Northfield, Vermont.
HOWARD, W. D. M. (Sept. 27, '16) Consult. Eng., Industrial Development Syndicate; mailing address, 840 Van Ness Ave., San Francisco, Cal.
HOWE, David (Sept. 27, '16) Foreman, Reed & Barton, 16 Rockland St., Taunton, Mass.
HOWE, Prof. Henry M. (Aug. 7, '02) Professor of Metallurgy, Columbia University, New York City; res., Broad Brook Road, Bedford Hills, N. Y.
HUBLEY, Warren F. (May 24, '13) Pres., American Transformer Co., 145 Miller St., Newark, N. J.
HUFFARD, Jno. B. (Sept. 25, '09) Metallurgist, Electro-Metallurgical Co., Glen Ferris, W. Va.
HULETT, Geo. A. (Apr. 2, '04) Princeton Univ., Princeton, N. J.
HUMBERT, Ernest P. (Mar. 27, '09) Box 26, Welland, Ontario, Canada.
HUNT, A. M. (Apr. 3, '02) Consult. Eng., 55 Liberty St., New York City.
HUNTER, J. Vincent (Jan. 28, '11) Gen. Foreman of Shops, Twin Cities St. Railways Co.; mailing address, 152 Arthur Ave., Minneapolis, Minn.
HUNTER, M. A. (Apr. 29, '11) Assistant Professor, Physics and Electrochemistry, Rensselaer Polytechnic Institute, Troy, N. Y.; res., 8 Whitman Court.
HUNTOON, Louis D. (May 27, '14) 115 Broadway, New York City.
HURUM, Fredrick (Nov. 26, '15) Carbon Steel Co., Pittsburgh, Pa.; mailing address, 510 Neville St.
HUTCHINGS, Chas. F. (June 27, '13) Gen. Mgr. North American Chemical Co., Bay City, Mich.
HUTCHINGS, James T. (Sept. 26, '08) Asst. Gen. Mgr., Rochester Ry. & Lt. Co., Rochester, N. Y.
HUTCHINS, Otis (Jan. 28, '11) Mentz Apartments, Niagara Falls, N. Y.
HYDE, Edward P. (Oct. 29, '08) Director, Nela Res. Lab., National Lamp Wks. of General Electric Co., Nela Park, Cleveland, Ohio.
HYDE, Reed W. (Oct. 22, '15) Res. Chem., American Smelt. and Refining Co., Murray, Utah.
IGARASHI, Tadao (Apr. 22, '15) Shimmachi, Komazawa-Mura, Ebara-Gun, Tokio, Japan.
IMLAY, Lorin E. (Dec. 31, '09) Superintendent, The Niagara Falls Power Co., Niagara Falls, N. Y.
INGALLS, Walter Renton (June 29, '07) 10th Ave. at 36th St., New York City.
ISAKOVICS, Alois von (Apr. 3, '02) Proprietor, Synfleur Scientific Laboratories, Monticello, N. Y.
ISHIKAWA, Ichiro (Oct. 22, '15) Chem. Eng., c/o Hooker Electrochemical Co., Niagara Falls, N. Y.
IWAI, Kyosuke (May 26, '10) Supt. Yusenji Copper Mine, Takeuchi Min. Co., Ltd.; mailing address, 31 Akashicho, Tsukiji, Tokyo, Japan.
JACOB, Arthur (Dec. 30, '16) Director, British Aluminium Co. Ltd.; res., Sterndale, Hatch End, Middlesex, England.
JACK, Geo. B., Jr. (Oct. 21, '16) Asst. Met., Maxwell Motor Co., 21 Edmund St., Dayton, Ohio.
JACKSON, Alf. Geo. (July 30, '09) Manager, Synchronome Electrical Co. of Australasia, Ltd.; res., 65 Ann St., Brisbane, Queensland, Australia.
JACOBSEN, Fredrik (Sept. 24, '10) Consulting Engineer, Kleven 22, Stavanger, Norway.
JACOBSON, B. H. (Mar. 24, '16) Student, Lehigh University, So. Bethlehem, Pa.; mailing address, 229 So. New St., Bethlehem, Pa.
JACOBY, Henry E. (Oct. 21, '16) Mech. Eng., 436 Convent Ave., New York City.
JAMES, Edgar T. (Apr. 27, '12) Chemist, 5861 Burchfield Ave., Pittsburgh, Pa.
JAMES, Dr. J. H. (Apr. 3, '02) Prof. of Chem. Eng., Chem. Dept., Carnegie Technical School, Pittsburgh, Pa.

JAMES, Wm. F. (Oct. 21, '16) Sales Eng., Westinghouse Elec. and Mfg. Co., 227 W. Mt. Pleasant Ave., Philadelphia, Pa.
JANSEN, E. W. (Oct. 22, '15) Gen. Mgr., Sec'y and Treas., Atlanta Welding Corp., 30 Church St., New York City.
JARVIS, Ernest G. (Sept. 27, '16) Chemist, c/o McNab & Harlin Mfg. Co., Paterson, N. J.
JENISTA, Prof. Geo. J. (Sept. 24, '10) Director of College of Engineering, De Paul University, Chicago, Ill.; mailing address, 3160 Abbott Court.
JENNISON, Herbert C. (Feb. 29, '08) with the American Brass Co., Ansonia, Conn.; mailing address, P. O. Box 600.
JEPPSON, Geo. N. (Sept. 4, '02) Norton Co., Worcester, Mass.
JESPERSON, C. M. (Aug. 25, '16) Eng., Anniston Steel Co., Birmingham, Ala.
JOHANSEN, G. H. (Aug. 27, '09) Civil Eng., Gen. Sec'y of Norwegian Water Power Co., Bankpladsen 1, Kristiania, Norway.
JOHNS, Morgan J. (June 25, '09) c/o Mount Morgan Gold Mining Co., Mount Morgan, Queensland, Australia.
JOHNSON, Arden R. (June 2, 06) 4313 Lincoln Ave., Chicago, Ill.
JOHNSON, Joseph A. (May 25, '12) Electrical Engineer, Ontario Power Co., Box 333, Niagara Falls, N. Y.
JOHNSON, J. E. Jr. (June 1, '15) Consult. Eng. & Met., 52 William St., New York City.
JOHNSON, Woolsey McA. (Apr. 3, '02) Pres., The Continuous Zinc Furnace Co., 599 Broad St., Hartford, Conn.
JOHNSTON, Frederick A. (Apr. 24, '09) Supt., Assay and Metallurgical Division, The S. S. White Dental Mfg. Co., Prince Bay, S. I., N. Y.
JOHNSTON, Wm. A. (Oct. 10, '03) Supt. of Mfg., S. S. White Dental Mfg. Co., Prince Bay, S. I., N. Y.
JONES, George H. (Oct. 29, '10) Power Engineer, Commonwealth Edison Co., Chicago, Ill.; res., 279 Keystone Ave., River Forest, Ill. (Oak Park, P. O.)
JONES, Grinell (Nov. 26, '10) Instructor in Chemistry; res., 11 Huron Ave., North Cambridge, Mass.
JONES, Harold (May 29, '09) Metallurgist, The St. John del Rey Gold Mining Co., Villa Nova de Lima, Minas Geraes, Brazil.
JORGENSEN, E. L. (Aug. 25, '16) Met. Eng., Guggenheim Bros.; mailing address, c/o Chile Exploration Co., Chuquicamata, Chile.
JOYCE, Clarence M. (May 1, '06) c/o J. Merritt Mathews, 50 E. 41st St., New York City.
KAHLENBERG, Louis, Ph. D. (Apr. 3, '02) Prof. of Phys. Chem., Univ. of Wis., Madison, Wis.; res., 234 Lathrop St.
KALMUS, Dr. Herbert T. (May 25, '12) Vice-Pres. and Treas., The Exolon Co., Cambridge, Mass.; mailing address, Kalmus, Comstock & Wescott, Inc., Engineers and Industrial Res. Chemists, 156 Sixth Street, Cambridge, Mass.
KAMEYAMA, Naoto (Dec. 31, '15) 10 Nishikatamachi, Hongo, Tokyo, Japan.
KÄMMERER, Jacob A. (Oct. 28, '09) President and Gen. Mgr., Wood Products Co. of Canada, Toronto, Canada; res.,, 87 Jameson Ave.
KAMMERHOFF, H. H. M. (Sept. 27, '16) Mgr. Carbolic Acid Mfg. Division, 159 Cleveland St., Orange, N. J.
KANEKO, Kiosuke (Sept. 27, '13) Prof. of Met., College of Engineering, Imperial Univ. of Kyushu, Fuknoka, Japan.
KAO, Takang (Dec. 30, '16) Graduate Apprentice, American Rolling Mill Co.; mailing address, c/o Chinese American Co., 136 Federal Bldg., Boston, Mass.
KARR, Corydon P. (Apr. 6, '11) Associate Physicist, c/o Bureau of Standards, Division of Metallurgy, Washington, D. C.
KATSURA, Prof. Benzo (May 29, '09) Professor of Metallurgy, The Imperial Tokyo University, Tokyo, Japan; res., 58 Sendaki-Machi, Hongo-Ku, Tokyo.
KAUFFMANN, F. A. (Aug. 25, '16) Chemist, The Roessler & Hasslacher Chem. Co., 44 Woodruff Place, Perth Amboy, N. J.
KAWAMURA, Takeshi (June 28, '12) Mining Dept., Mitsubishi Co., Tokyo, Japan.
KAWIN, Chas. C. (Nov. 6, '10) Advising Metallurgist, Chas. C. Kawin Company, Chicago, Ill.; res., 417 S. Dearborn St.
KEEN, Wm. Herbert (Aug. 25, '16) Met. Supt., Washington Steel and Ordnance Co., Box 1812, Washington, D. C.; mailing address, 3210 34th St., N. W.
KEENEY, Robt. M. (Nov. 24, '11) Mgr., The Ferro Alloy Co., Denver, Colo.; mailing address, 1418 Elizabeth St.
KEFFER, Frederick (Feb. 27, '09) Cons. Eng. and Geologist, 610 Hutton Bldg., Spokane, Wash.
KEITH, Dr. N. S. (April 3, '02) 350 Bullitt Bldg., Philadelphia, Pa.
KELLER, Ch. A. (June 25, '09) Genl. Mgr., Keller-Leleux Cie., 3 Rue Vignon, Paris, France.
KELLER, Ed. (Apr. 3, '02) Chief of Chem. & Sampling Dept., Raritan Copper Works, Perth Amboy, N. J.; mailing address, P. O. Box 363.
KELLER, Oran (Oct. 23, '14) Chemist, U. S. Metals Ref. Co., 253 George St., New Brunswick, N. J.
KELLY, Dr. John F. (Apr. 3, '02) Stanley Elec. Mfg. Co.; res., 284 W. Housatonic St., Pittsfield, Mass.
KELLOGG, Harry W. (Jan. 29, '09) Genl. Mgr., National Electrolytic Co., Niagara Falls, N. Y.

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KEMERY, Philo (May 29, '09) Metallurgical Engineer, Crescent Works, Crucible Steel Co. of America, Pittsburgh, Pa.
KEMMER, Frank R. (Feb. 25, '11) Supt., The Aluminum Co. of America, Whitney, North Carolina.
KEMPER, David A. (Oct. 21, '16) Chemist, Marden, Orth & Hastings, Newark, N. J.; mailing address, 1144 President St., Brooklyn, N. Y.
KENAN, Wm. R. (Apr. 3, '02) 433 Locust St., Lockport, N. Y.
KENNEDY, A. M. (Sept. 27, '16) Staff Eng., Edison Lab., Orange, N. J.
KENNEDY, J. J. (May 9, '03) Engineer, 52 Broadway, New York City.
KENNEDY, T. O. (Apr. 26, '16) Gen. Mgr., The Mass. Electric & Gas Co., Massillon, Ohio.
KENNEY, Edward F. (Feb. 26, '10) Metallurgical Engineer, Cambria Steel Co., Johnstown, Pa.
KENRICK, Frank B. (Apr. 26, '13) Associate Prof. Chem., Univ. of Toronto, Toronto, Canada; res., 77 Lonsdale Road.
KENT, Jas. M. (Sept. 4, '03) Consult. Eng. and Teacher and Engineer of Applied Steam and Electricity, Manual Training School, 2446 Harrison St., Kansas City, Mo.
KERN, Ed. F., Dr. (Apr. 4, '03) c/o Dept. of Metallurgy, Columbia Univ., New York City.
KERN, P. E. (Nov. 24, '11) 419 N. Central Park Blvd., Chicago, Ill.
KIER, Samuel M. (Oct. 29, '08) Pres., Kier Firebrick Co., 2243 Oliver Bldg., Pittsburgh, Pa.
KINNEAR, H. B. (Aug. 25, '16) Metallurgist, Whitaker-Glessner Co.; mailing address, 1918 Summit St., Portsmouth, Ohio.
KINTER, Geo. R. (Mar. 24, '16) Student, Lehigh University, Section A, Taylor Hall, South Bethlehem, Pa.
KISHI, Keijiro (Nov. 21, '08) Chief Eng., El. Dept., Shibaura Eng. Wks., No. 1, Shinhamacho, Kanasugi, Shibaku, Tokyo, Japan.
KISSOCK, Alan (Sept. 20, '11) 79 Wall St., New York City.
KITSEE, Dr. Isador (Apr. 3, '02) 306 Stock Exchange Place, Philadelphia, Pa.
KLEINFELDT, Henry F. (Apr. 22, '15) Sec'y, Abbe Engineering Co., 121 Park Ave., Newark, N. J.
KLIPSTEIN, Ernest C. (Apr. 3, '02) 122 Pearl St., P. O Box 2833, New York City; res., 116 Prospect St., East Orange, N. J.
KNAPP, Geo. O. (Nov. 6, '02) 42d St. Bldg., New York City.
KNIFFIN, L. M. (Aug. 25, '16) Asst. Supt., U. S. Metals Ref. Co., 4817 Baring Ave., East Chicago, Ind.
KNIGHT, Frank P. H. (Feb. 25, '11) Electrician, Chemist, Inventor, Electric Service Supplies Co., Keokuk, Iowa; res., 1015 Blondean St.
KNOEDLER, E. L. (Dec. 30. '16) Gen. Supt., Welsbach Co.; mailing address, 110 Brown St., Gloucester City, N. J.
KNOX, Lester B. (Mar. 24, '16) Supt., John A. Crowley Co.; mailing address, 1203 West Grand Boulevard, Detroit, Mich.
KOCH, Stanley B. (May 29, '09) 137 S. Fourth St., Steelton, Pa.
KOEHLER, Wm. (Nov. 5, '04) E. 792 Lakeview Road, N. E., Cleveland, Ohio.
KOERING, Bruno K. (Sept. 27, '16) Pres. and Gen. Mgr., Koering Cyanide Process Co.; mailing address, 511 Hammond Bldg., Detroit, Mich.
KOERNER, Walter E. (May 27, '14) Electrochemist and Metallurgist, General Elec. Co.; mailing address, 255 Amherst St., East Orange, N. J.
KOETHEN, Frederick L. (Jan. 29, '10) Chemist, International Acheson Graphite Co., Niagara Falls, N. Y.; mailing address, 1960 Whitney Ave.
KOHLER, Hy. L. (Aug. 31, '07) Monsanto Chem. Co., res., 2315 Ann Ave., St. Louis, Mo.
KOHN, Milton M. (May 29, '09) Mgr., Multiple Unit Electric Co., 136 Liberty St., New York City.
KOLKIN, T. L. (Oct. 27, '11) Mgr., A/s Vadheim Elektromiske Fabriker, Vadheim, Sogne, Norway.
KOONTZ, John A., Jr. (Sept. 27, '16) E. E., Great Western Power Co., 221 Bryant St., Palo Alto, Cal.
KOWALKE, O. L. (Aug. 3, '06) Assoc. Prof. of Chem. Eng., Univ. of Wis., Chem. Eng. Bldg., Madison, Wis.
KRAMER, Lewis B. (Mar. 24, '16) Student, Lehigh University, So. Bethlehem, Pa.; mailing address, A. 14, Taylor Hall.
KRANZ, Wm. G. (Apr. 29, '11) Mgr. Sharon and Melrose Park Works, Sharon, Pa.; mailing address, National Malleable Castings Co.
KRAUS, Ernest (Sept. 27, '13) Res. Chem., 40-A Eldorado Place, Weehawken, N. J.
KRAUSE, Walter B. (Apr. 24, '14) 2920 Virginia Place, East St. Louis, Ill.
KREJCI, Milo W. (May 27, '09) Anaconda Copper Mining Co., Boston and Montana Reduction Wks., Great Falls, Mont.; mailing address, 15 Smelter Hill.
KREMERS, J. G. (July 31, '07) 906 Shepherd Ave., Milwaukee, Wis.
KROG, Karl M. (June 30, '16) Shift Supt., Electrolytic Tank House, c/o Chile Exploration Co., Chuquicamata, Chile.
KUNZ, Geo. F., Ph. D., D. Eng. (Sept. 28, '07) Gem Expert, Tiffany & Co., 401 Fifth Ave., New York City.
KUTZ, Milton (June 1, '15) Mgr., The Roessler and Hasslacher Chem. Co., 941 Drexel Bldg., Philadelphia, Pa.

KWANG, Kwong Yung, D. Eng. (Apr. 24, '09) Engineer and Director, Lincheng Mines, Lincheng, via Pekin, N. China.
KYLE, T. D. (Apr. 3, '02) 106 E. 5th St., Leadville, Colo.
LACEY, Wm. Noble (Dec. 28, '12) 921 A Ave., Coronado Beach, Cal.
LACROIX, Henry (Mar. 3, '06) Eng., Usine de Degrossissage d'or, Geneve, Switzerland.
LAFORE, J. A. (Apr. 3, '02) 25th and Locust Sts., Philadelphia, Pa.; res., Wister Road, Ardmore, Pa.
LAIB, Walter (May 22, '14) Chem. Eng., The Ohio Salt Co., Wadsworth, Ohio; mailing address, Rittman, Wayne Co., Ohio.
LAMB, Arthur B. (Dec. 27, '07) Chemical Lab., Harvard College, Cambridge, Mass.
LAMKER, H. G. (May 24, '13) 18 Maud St., Pittsfield, Mass.
LANDAU, Alfred (Apr. 22, '15) Pres., Canadian Carbon Co., Ltd., United Battery Corp. of N. Y., Woolworth Bldg., New York City.
LANDIS, Walter S. (Dec. 4, '02) Chief Technologist, American Cyanamid Co., New York; mailing address, East 31st St., Beechurst, L. I., New York.
LANDOLT, Dr. Hans (Feb. 5, '03) Turgi, Switzerland.
LANDOLT, P. E. (Nov. 27, '14) Chemical Eng., Research Corp., 63 Wall St., New York City; mailing address, 625 Ditmas Ave., Brooklyn, N. Y.
LANE, Henry M. (May 29, '09) Trussed Concrete Bldg., Detroit, Mich.
LANGFORD, Frank (May 29, '09) 1112 J St., Eureka, Humboldt County, Cal.
LANGMUIR, Irving (June 29, '07) Research Lab., Genl. Elec. Co., Schenectady, N. Y.
LANGTON, John (Apr. 3, '02) 233 Broadway, New York City.
LANSING, C. N. (Nov. 26, '15) Eng. on Cells, Hooker Electrochemical Co., Niagara Falls, N. Y.
LARCHAR, Arthur B. (Apr. 3, '02) Penobscot Chem. Fibre Co., Great Works, Me.
LASS, W. P. (Mar. 27, '09) Speel River Electrochemical Co., Juneau, Alaska.
LATHROP, L. H. (Sept. 26, '08) General Supt., Ironwood & Bessemer Ry. & Light Co., Ironwood, Mich.
LAUGHLIN, H. Hughart (May 29, '09) Elec. Engr., Jones & Laughlin Steel Co., 2709 Carson St., Pittsburgh, Pa.; res., 5023 Bayard St.
LAVENE, H. A. (Nov. 26, '15) Chemist, International Acheson Graphite Co.; mailing address, 21 Mentz Apts., Niagara Falls, N. Y.
LAVINO, Edward J. (Nov. 26, '07) E. J. Lavino & Co., Importers of Ferro-Alloys, Bullitt Bldg., Philadelphia, Pa.
LAWRENCE, J. N. (Feb. 23, '12) 15 Fargo Ave., Buffalo, N. Y.
LAY, J. Tracy (Nov. 26, '10) Graduate Student, University of Pennsylvania, Philadelphia, Pa.; res., 4015 Pine St.
LEACH, Edwin R. (Feb. 25, '11) Mgr. Island Copper Co., 716 Security Bank Bldg., Oakland, Cal.; mailing address, 217 Hillside Ave., Piedmont, Cal.
LEAVITT, Wm. F. B. (Mar. 26, '10) c/o C. W. Leavitt & Co., 30 Church St., New York City.
LEBHERZ, John (Mar. 24, '16) President, Frontier Brass Foundry, 937-44 Elmwood Ave., Niagara Falls, N. Y.
LE BOUTILLIER, Clement (July 31, '08) Chem. and Met., Katonah, N. Y.
LEDOUX, Albert R. (July 25, '13) Eng. and Chemist, Pres., Ledoux & Co., Inc., 99 John St., New York City.
LEE, Harry R. (Dec. 2, '05) Holcomb's Rock, Va.
LEE, I. E. (Mar. 24, '16) Instructor in Chemistry, University of Rochester, N. Y.
LEFFEL, C. E. (Sept. 25, '14) Supt., The Spirella Co., Inc., Box 127, Niagara Falls, N. Y.
LEFFLER, Johan A. (Sept. 24, '10) Technical Gen. Director, Gimo-Österby Bruks Aktiebolag, Osterby Bruk, Dannemora, Sweden.
LEGRAND, Charles (Mar. 24, '16) Consult. Eng., Phelps Dodge Co.; mailing address, P. O. Box EE, Douglas, Ariz.
LEMBERG, Max (Apr. 6, '11) Chief Engr., Vulcan Detinning Co., Sewaren, N. J.; res., Woodbridge, N. J.
LEONARD, Grover M. (Sept. 27, '16) Store Keeper, The Jeffrey Mfg. Co.; mailing address, 1225 Wesley Ave., Columbus, Ohio.
LESLIE, E. H. (Sept. 27, '16) Chief Chemist, General Petroleum Corp.; mailing address, 4045 Brighton Ave., Los Angeles, Cal.
LETCHFIELD, F. T. (June 26, '14) Engineer of Construction, Thousand Springs Power Co., Salt Lake City, Utah; mailing address, 46 So. State St.
LEWIS, Jonathan D. (May 29, '09) Chemist, Edgar Thompson Wks., Carnegie Steel Co.; mailing address, 710 Middle St., Braddock, Pa.
LICHTHARDT, G. (Apr. 3, '02) 18th and M. Sts., Box 510, Sacramento, Cal.
LIDBURY, F. Austin (Aug. 7, '03) Works Mgr., Oldbury Electrochem. Co.; res., 33 Sugar St., Echota, Niagara Falls, N. Y.
LIEBMANN, Dr. A. J. (Aug. 26, '10) 55 W. 95th St., New York City.
LIEBSCHUTZ, Morton (Jan. 28, '11) Analytical Chemist, The Balbach Smelt. and Ref. Co., Newark, N. J.; res., 719 De Graw Ave.
LIHME, C. B. (Nov. 27, '09) Director Matthiessen & Hegeler Zinc Co.; mailing address, 1200 Lake Shore Drive, Chicago, Ill.
LILJENROTH, F. G. (Dec. 31, '15) Consult. Eng., c/o Engineering Dept., duPont Co., Wilmington, Del.

LINCOLN, Dr. A. T. (Nov. 6, '02) Prof. of Physical Chemistry, Rensselaer Polytechnic Institute, Troy, N. Y.; mailing address, 1625 Tibbitts Ave.
LINCOLN, Edwin S. (Sept. 26, '08) Consult. Eng., 25 Silver St., Waterville, Maine.
LINCOLN, P. M. (Apr. 3, '02) 6830 Thomas St., Pittsburgh, Pa.
LIND, S. C. (July 30, '09) Chem. in Radioactivity, U. S. Bureau of Mines, Golden, Colo.
LINDBERG, Sven C. son (Sept. 27, '13) Tech. Mgr., Stierns Aktiebolag, Vddeholm, Sweden.
LINDSAY, Dr. Chas. F. (June 1, '07) Imperial Munitions Board, Transportation Bldg., Ottawa, Canada.
LISCOMB, Fred. J. (Feb. 25, '16) Salesman, Hanson & Van Winkle Co., 6066 Nickerson Ave., Chicago, Ill.
LITTLE, Arthur D. (Apr. 1, '05) Chem. Eng. and Expert, 93 Broad St., Boston, Mass.
LITTLE, Wm. T. (Mar. 24, '16) Research Dept., Al. Co. of America, Box 35, Massena, N. Y.
LJUNGH, Hjalmar (Mar. 27, '09) W. Ropes & Co., Petrowsky, Petrograd, Russia.
LLOYD, M. G., Ph.D. (Apr. 3, '02) 1040 Ontario St., Oak Park, Ill.
LLOYD, Sherman C. (Sept. 26, '08) 1402 Gilpin Ave., Wilmington, Del.
LLOYD, Stewart J. (Oct. 28, '09) Professor of Metallurgy and Chem., University of Alabama, University, Ala.
LOEBELL, Henry O. (Aug. 28, '14) Industrial Heating Expert, Henry L. Doherty & Co., 60 Wall St., New York City.
LOEFFLER, Geo. O. (Mar. 24, '16) Metallurgist, Carbon Steel Co.; mailing address, 325 South Pacific Ave., Pittsburgh, Pa.
LOHR, J. M. (May 24, '13) Alloy Chemist, U. S. Bureau of Mines, Morse Hall, Ithaca, N. Y.
LOKEN, Rikard (Nov. 26, '15) Chemist, Kristianssand Nikkelraffineringsverk, Kristianssand S, Norway.
LONG, Geo. E. (Jan. 28, '08) 732 W. Washington St., Napoleon, Ohio.
LORD, Chas. E. (Jan. 29, '10) care of International Harvester Co., 606 S. Michigan Ave., Chicago, Ill.
LOVE, Edward G. (May 29, '09) Chief Chemist, Consolidated Gas Co., 130 E. 15th St., New York City.
LOVEJOY, D. R. (Apr. 3, '02) U. S. E. M. Co., 221 W. 33d St., New York City.
LOVELACE, B. F. (Oct. 27, '11) Associate Prof. of Chemistry, Johns Hopkins University, Baltimore, Md.
LOVERIDGE, F. H. (Dec. 31, '09) Electrical Engineer, 954 Monadnock Bldg., Chicago, Ill.
LOW, Frank S. (Apr. 26, '16) Chem. Eng., The Weaver Co., 720 Williamson St., Madison, Wis.
LUCAS, Anthony F. (April 6, '11) 2300 Wyoming Ave., Washington, D. C.
LUCKE, Henry J. (June 6, '03) Mastick & Lucke, 2 Rector St., New York City.
LUKENS, Hiram S. (Feb. 27, '14) Asst. Prof. of Chem., John Harrison Lab. of Chemistry, Univ. of Pa., Philadelphia, Pa.
LUNDGREN, Harald (Aug. 25, '11) 7742 Marquette Ave., Chicago, Ill.
LUNN, Ernest (Jan. 29, '09) The Pullman Co., Room 801, Pullman Bldg., Chicago, Ill.
LYMAN, James (Apr. 3, '02) Firm of Sargent & Lundy, 1412 Edison Bldg., Chicago, Ill.
LYON, Dorsey A. (Feb. 27, '09) Met., U. S. Bureau of Mines, Univ. of Washington, Seattle, Wash.
LYONS, Henry N. (Oct. 21, '16) Charge of Acid Recovery Operation, Hercules Powder Co., Kenvil, N. J.
LYSTER, T. L. B. (Nov. 26, '15) Eng., Hooker Electrochemical Co., Niagara Falls, N. Y.
MAC DONALD, Jas. A. (Aug. 7, '03) Vice-Pres., United Verde Copper Co., 26 Exchange Place, New York City.
MAC GREGOR, Frank S. (Sept. 28, '07) Development Dept., Room 452, Du Pont Bldg., Wilmington, Del.
MAC GREGOR, Walter (Jan. 29, '10) Supt., Timken Detroit Axle Co., Clark St., Detroit, Mich.; mailing address, 407 W. Grand Boulevard, Detroit, Mich.
MAC INNES, Duncan A. (Jan. 25, '13) Instructor in Chemistry, Chemical Lab., Univ. of Ill., Urbana, Ill.
MAC MAHON, Jas. (Aug. 7, '02) Bleaching Powder Supt., Castner Electrolytic Alkali Co., Niagara Falls, N. Y.
MAC MAHON, J. Douglas (Aug. 25, '16) Asst. in Res. Dept., Norton Co.; mailing address, 15 Ericsson Place, Niagara Falls, N. Y.
MAC MILLAN, J. R. (Oct. 23, '14) Chemist, Niagara Falls Alkali Co., 428 11th St., Niagara Falls, N. Y.
MAC NUTT, Barry, E.E., M.S. (Apr. 3, '02) Phys. Lab., Lehigh Univ., South Bethlehem, Pa.
MADSEN, Chas. P. (Oct. 22, '15) Res. Engineer, Driver-Harris Wire Co., 44 Walnut St., Newark, N. J.
MAGNUS, Benjamin (Apr. 3, '02) Consult. Eng., c/o Adolph Lewisohn & Sons, 61 Broadway, New York City.

MAIER, Chas. G. (Dec. 31, '14) Res. Chemist, c/o Phelps, Dodge Co., 99 John St., New York City.
MAILLOUX, C. O., D.Sc. (Apr. 3, '02) 20 Nassau St., New York City.
MAIN, Wm. (Apr. 3, '02) Piermont, Rockland Co., N. Y.
MAINWARING, Wm. D. (Apr. 24, '14) Production Engineer, 866-70 Rockefeller Bldg., Cleveland, Ohio.
MALINOVSZKY, Andrew (Oct. 21, '16) Chief Chem., American Brick Co., Lincoln, Ill.
MALM, John L. (Aug. 5, '05) Electrochemical Eng., 1022 1st Nat. Bank Bldg., Denver, Colo.
MANAHAN, Paul R. (Apr. 30, '08) 70 Cedar St., Roxbury, Mass.
MANGER, Fird W. (Apr. 2, '13) Mgr., 47 Bentley Ave., Jersey City, N. J.
MANN, Wallace W. (May 5, '10) Foreman, Battery Department, The National Carbon Co., Cleveland, Ohio; res., 1369 Summit Ave., Lakewood, Ohio.
MANNHARDT, Hans (Jan. 28, '11) Chief Chemist, Heath-Milligan Mfg. Co., 170 Randolph St., Chicago, Ill.; res., 1104 Oakdale St.
MANTIUS, Otto (Jan. 28, '08) Consult. Eng., Woolworth Bldg., New York City.
MARIE, Charles, Dr. des Sciences (Jan. 8, '04) 9 rue de Bagneux, Paris, VI, France.
MARSH, A. L. (May 29, '09) Chief Engineer, Hoskins Mfg. Co., Detroit, Mich.
MARSH, Clarence W. (Dec. 26, '08) Consult. and Chem. Eng., 201 Devonshire St., Boston, Mass.; mailing address, 15 Herrick St., Winchester, Mass.
MARSH, Geo. E. (Oct. 28, '09) Asst. Prof. in Electrical Engineering, Armour Inst. of Tech., Chicago, Ill.
MARSH, R. J. (Sept. 27, '16) Chemist and Asst. Supt., c/o R. Wallace & Son Mfg. Co., Wallingford, Conn.
MARSHALL, Jas. G. (Sept. 2, '04) Asst. Supt. Union Carbide Co.; res., 1115 Niagara St., Niagara Falls, N. Y.
MARTIN, Thos. C. (Feb. 26, '10) 42 Morningside Ave., New York City.
MARVIN, Arba B., Jr. (Apr. 3, '02) c/o J. C. Pennie, 35 Nassau St., New York City.
MASON, Frederic S. (July 21, '11) 92 Beekman St., New York City.
MASON, Wm. D. (Aug. 25, '11) Chief Electrician, c/o Standard Oil Co., Point Richmond, Cal., Box 394, Pt. Richmond, Cal.
MASTICK, Seabury C. (Feb. 27, '09) Mastick & Lucke, 2 Rector St., New York City.
MASUJIMA, Bunjiro (Mar. 4, '05) c/o K. Takebe, No. 16 Gazenbo-cho, Azabuku, Tokyo, Japan.
MATHERS, Frank C. (Feb. 6, '04) 419 N. Indiana Ave., Bloomington, Ind.
MATHEWS, Dr. John A. (May 29, '09) Pres. and Gen. Mgr., Halcomb Steel Co., Syracuse, N. Y.
MATHEWSON, E. P. (May 27, '14) Royal Bank Bldg., 8 King St., East, Toronto, Canada.
MATHIAS, D. L. (Jan. 28, '16) Metallurgist, c/o Mackintosh-Hemphill & Co., 803 Manufacturers Bldg., Pittsburgh, Pa.
MATTERN, Guy G. (Aug. 25, '16) Westinghouse Elec. & Mfg. Co., 780 Ellicott Square, Buffalo, N. Y.
MAUELEN, Frederick (June 25, '09) Baker & Co., Inc., Newark, N. J.; mailing address, 79 W. Hazelwood Ave., Rahway, N. J.
MAURAN, Max (Nov. 6, '02) Eng. and Asst. Mgr., Castner Electrolytic Alkali Co., Niagara Falls, N. Y.
MAYS, S. Warren (Apr. 22, '15) Room 540, No. 200 Fifth Ave., New York City.
McADAM, D. J., Jr., Ph. D. (Jan. 29, '10) Metallographist, Engineering Experiment Station, Annapolis, Md.
McBERTY, Ford H. (Aug. 25, '16) Student in E. E., Cornell Univ., Bandhu, The Knoll, Ithaca, N. Y.
McBERTY, Frank R. (Sept. 25, '09) c/o Western Elec. Co., Ltd., Norfolk House, Victoria Embankment, London, W. C., England.
McCLENAHAN, J. S. (June 30, '16) Asst. Supt., Electrolytic Tank House, Chile Exploration Co., Via Antofagasta, Chuquicamata, Chile.
McCONNELL, J. Y. (Apr. 3, '02) 500 N. Broad St., Philadelphia, Pa.; res., Colwyn, Pa.
McCORMACK, Harry (June 29, '07) Associate Prof., Dept. of Chemical Engineering, Armour Inst., Chicago, Ill.
McCOY, Herbert N. (Sept. 4, '03) Kent. Chem. Lab., Univ. of Chicago, Chicago, Ill.
McCULLOUGH, H. F. (Apr. 29, '11) 1114 Turner St., Allentown, Pa.
McDONALD, Frank (Apr. 29, '11) Supt., Electrolytic Plant, D. M. Bare Paper Co., Roaring Springs, Pa.
McDONALD, Robert A. (June 25, '10) Manager, Crescent Steel Co., Crucible Steel Co. of America, Pittsburgh, Pa.; res., 304 S. Fairmount Ave.
McGALL, Edward (Oct. 27, '11) Electrochemical Eng., Primary Batteries, Thos. A. Edison Co., Inc., Bloomfield, N. J.
McINTOSH, D. (Dec. 4, '02) The University of British Columbia, Vancouver, B. C., Canada.
McKEE, Geo. M. (Aug. 7, '03) Donnacona, Quebec, Canada.
McKELVY, Ernest C. (Aug. 27, '09) Associate Chemist, Bureau of Standards, Washington, D. C.

McKINLEY, Joseph (May 26, '10) Power Salesman, The Allegheny County Light Co., 435 Sixth Ave., Pittsburgh, Pa.
McKNIGHT, W. A. (Apr. 22, '15) Chem. Eng., Ass't in Operating Dept., Aluminum Co. of America, Niagara Falls, N. Y.
McLAUGHLIN, Dorsey E. (May 27, '11) 904 Union Oil Bldg., Los Angeles, Cal.
McNEILL, Ralph (Feb. 5, '03) 223 W. 106th St., New York City.
McNIFF, Gilbert P. (June 25, '10) Metallurgical Eng., Shelby Steel Tube Co., Frick Bldg., Pittsburgh, Pa.; res., 896 Eighth Ave.
McNITT, Robt. J. (Mar. 24, '16) Asst. Vice-Pres., The Roessler and Hasslacher Chem. Co., Perth Amboy, N. J.
MEAKER, Guy L. (July 24, '14) Pres., The Meaker Co., Chicago, Ill.; mailing address, 311 Campbell St., Joliet, Ill.
MEDBURY, C. F. (Oct. 22, '15) Mgr. Montreal Office, Canadian Westinghouse Co., Montreal, Quebec, Canada.
MEGROOT, J. P. (Nov. 24, '16) Electrochem. Eng., 2127 W. 48th St., Cleveland, Ohio.
MEINEKE, Otto H. (Sept. 27, '16) Construction Electrician, 422 Park Road, Ambridge, Pa.
MELCHER, A. C. (July 3, '02) Purchasing Agent for Dept. of Chemistry, Mass. Inst. of Tech., Cambridge, Mass.; res., 58 Bowen St., Newton Centre, Mass.
MEREDITH, William F. (May 29, '09) Titanium Alloy Mfg. Co., Niagara Falls, N. Y.
MERRILL, Chas. W. (Feb. 27, '14) Pres., Merrill Metallurgical Co., 121 Second St., San Francisco, Cal.
MERRILL, Millard W. (Apr. 26, '13) Electrolytic Tank House, c/o Chile Copper Co., Chuquicamata, Chile, South America.
MERSHON, Ralph D. (July 1, '05) Consulting Engr., 65 W. 54th St., New York City.
MERZ, Chas. H. (Apr. 3, '02) Consult. Eng., 32 Victoria St., Westminster, London, S. W.; Collingswood Bldgs., Newcastle-upon-Tyne, England.
MERZBACHER, Aaron (June 25, '09) 6622 Torresdale Ave., Tacony, Phila., Pa.
METZ, Gustave P. (Apr. 6, '11) Supt., Consolidated Color and Chemical Co., Lister Ave. and Brown St., Newark, N. J.; res., 95 Elm St., Montclair, N. J.
METZ, H. A. (Apr. 3, '02) 122 Hudson St., New York City.
MEYER, John (Oct. 7, '05) Eng. of Commercial Dept., Philadelphia Elec. Co., 1000 Chestnut St., Philadelphia, Pa.; res., 6420 Woodland Ave.
MEYER, Richard (Aug. 25, '16) Foreman, The Massillon Aluminum Co., 532 Cherry Ave., S. E., Canton, Ohio.
MEYERS, Herbert H. (June 26, '14) Res. Chemist, Mellon Inst. for Industrial Res., Pittsburgh, Pa.
MILLER, Daniel (Feb. 25, '16) Chemist, Barber Asphalt Co.; mailing address, 35 Bryant Terrace, Rahway, N. J.
MILLER, Levi B. (Jan. 29, '09) El. Chemist, General Electric Co., Harrison, N. J.; mailing address, 188 Washington St., Lynn, Mass.
MILLER, L. F. (Aug. 22, '13) 5107 Kimbark Ave., Chicago, Ill.
MILLER, Dr. W. Lash (Apr. 3, '02) 50 St. Albans St., Toronto, Canada.
MILLS, J. E., Ph. D. (Apr. 16, '03) Science Hall, University of South Carolina, Columbia, S. C.
MINDELEFF, Chas. (Aug. 26, '10) Chief Chemist and Assayer, American Smelting and Refining Co., Maurer, N. J.; res., Perth Amboy, N. J.
MINER, H. S. (May 1, '07) Chief Chemist, Welsbach Light Co., Gloucester City, N. J.
MOERK, Frank N. (Apr. 22, '15) Chem. Eng., N. W. Cor. 13th St. and Chelten Ave., Oak Lane, Philadelphia, Pa.
MOFFAT, Jas. W. (Apr. 29, '11) President, Moffat-Irving Electric Smelters, Ltd., 366 Sackville St., Toronto, Canada.
MOHN, Arnold (Aug. 25, '16) Electrochemist, River Smelting & Ref. Co., 214 N. 9th St., Keokuk, Iowa.
MOHR, Louis (Oct. 29, '10) Pres., John Mohr & Sons, 349 West Illinois St., Chicago, Ill.
MOLDENKE, Richard (Jan. 29, '09) Sec'y and Treas., Am. Foundrymen's Assoc., Watchung, N. J.
MOLTKEHANSEN, Ivar J. (Jan. 6, '03) Gen. Mgr., Fredriksstad Electrochemiske Fabriker, Fredriksstad, Norway.
MONTGOMERY, Jack P. (Feb. 21, '13) Adjunct Prof. of Chem., Univ. of Ala., University, Alabama.
MOODY, Dr. Herbert R. (June 29, '07) College of the City of New York, Chemical Bldg., New York City; res., 330 Convent Ave.
MOORE, Herbert S. (Oct. 22, '15) Asst. to E. E. Electrical Eng. Office, Ft. Dodge, Des Moines & Southern R. R., Boone, Iowa.
MOORE, Hugh K. (Feb. 25, '16) Chem. Eng., Berlin Mills Co., 93 Prospect St., Berlin, N. H.
MOORE, J. R. (Jan. 28, '16) Electrometallurgist, Oakmont, Pa.
MOORE, Wm. C. (Feb. 27, '14) Res. Chemist, National Carbon Co., Cleveland, Ohio; mailing address, 1581 Clarence Ave., Lakewood, Ohio.
MOORE, W. E. (Sept. 27, '16) Pres., W. E. Moore & Co., Cons. Engrs., 706 Union Bank Bldg., Pittsburgh, Pa.

MORDEN, Dr. G. W. (Feb. 27, '09) Manitoba Agricultural College, Manitoba, Winnipeg, Canada.
MOREHEAD, J. M. (Feb. 5, '03) Engineer of Tests, Peoples Gas Bldg., Chicago, Ill.
MORELAND, Watt L. (Apr. 26, '16) Gen. Mgr., Moreland Motor Truck Co., 1701 N. Main St., Los Angeles, Cal.
MOREY, S. R. (Apr. 29, '11) c/o Mr. F. M. Waltz, Jr., 4241 Broadway, New York City.
MORGAN, Harry J. (Sept. 27, '16) Metallurgist, c/o Big Indian Co., La Sal, Utah.
MORGAN, Dr. J. L. R. (Apr. 3, '02) Columbia Univ., New York City.
MORGAN, Leonard P. (Aug. 29, '08) 2003 Pine St., Philadelphia, Pa.
MORITZ, C. H. (Apr. 4, '03) c/o Aluminum Co. of America, Niagara Falls, N. Y.
MORRISON, Geo. O. (June 26, '14) Detroit Gas Co., Gas Office Bldg., Detroit, Mich.
MORRISON, M. E. (June 1, '15) 74 W. Beau St., Washington, Pa.
MORRISON, Walter L. (Feb. 26, '10) Supt. Electric Reduction Co., Washington, Pa.; 402 Ridge Ave., Canonsburg, Pa.
MORROW, John T. (Feb. 27, '09) c/o Factory Products Export Corp., 61 Broadway, New York City.
MORSE. Willard S. (Jan. 29, '09) Dir. and Mem. Ex. Comm., Am. Smelting and Ref. Co., 120 Broadway, New York City.
MORTIMER, James D. (Dec. 30, '16) Pres., The North American Co., 30 Broad St., New York City.
MOTT, W. R. (Mar. 5, '03) Nat. Carbon Co., Cleveland, Ohio; mailing address, 1586 Cohasset Ave., Lakewood, Ohio.
MOTTINGER, B. T. (Apr. 24, '14) Chief Eng., Boone, Iowa.
MOULTON, Seth A. (Apr. 29, '11) Consult. and Designing Engr., c/o The Moulton Engineering Corp., 120 Exchange St., Portland, Me.
MOYER, Grant C. (Jan. 29, '09) Lab. Asst., FitzGerald Labs., Niagara Falls, N. Y.
MUENCH, Reinbold K. (Nov. 24, '16) P. O. Box 293, Goldfield, Colo.
MUESER, Emil (Feb. 25, '16) Supt. Wks. No. 1, Aluminum Co. of America; mailing address, 170 Buffalo Ave., Niagara Falls, N. Y.
MUIR, J. Malcolm (Mar. 26, '10) Mgr., Metallurgical and Chemical Engineering, 239 W. 39th St., New York City.
MULLIGAN, J. J. (Oct. 23, '14) Asst. Chem., U. S. Metals Ref. Co.; mailing address, 111 Gordon St., Perth Amboy, N. J.
MURAHASHI, Sokichi (Nov. 24, '11) Met. Eng., Sokichi Murahashi Kawara Mura, near Kobe, Japan.
MURPHY, Edwin J. (Oct. 2. '02) 38 Ray St., R. D. No. 1, Schenectady, N. Y.
MURPHY, Dr. Robt. K. (May 22, '14) Technical College, Sydney, Australia.
MURRAY, Benjamin L. (Nov. 27, '09) Chemist, Merck & Co., Rahway, N. J.; mailing address, 148 Bryant St.
MURRAY, Henry T. (Apr. 24, '09) Chemist, Hayden Plant, American S. and R. Co., Hayden, Ariz.
MUSCHENHEIM, Frederick A. (Nov. 21, '08) Vice-Pres., Hotel Astor, New York City; res., 218 W. 45th St.
MYERS, Wm. S. (Feb. 25, '16) Director Chilean Nitrate Propaganda, 25 Madison Ave., New York City.
NAGELVOORT, Adriaan (Oct. 22, '15) Chemist, 52 E. 41st St., New York City.
NAMBA, M. (Nov. 6, '03) Prof. of Elec. Eng., Kyoto Imp. Univ., Kyoto, Japan.
NASH, Clarence A. (Jan. 25, '13) 1109 E. 62d St., Chicago, Ill.
NATHAN, A. F. (Mar. 27, '14) Patent Lawyer, Liberty Tower, 55 Liberty St., New York City.
NEEDHAM, Harry H. (Mar. 26, '15) Engineer, General Elec. Co., Harrison, N. J.; mailing address, 48 Telford St., East Orange, N. J.
NEES, A. R. (Oct. 22, '15) Chemist, Nat. Lead Co., Brooklyn, N. Y.; mailing address, 129 York St.
NESTLER, G. A. (Nov. 24, '16) Mill Foreman, Baker Mine Co., Cornucopia, Oregon.
NEUHAUS, R. (Nov. 26, '15) Works Mgr., Electric Bleaching Co., Niagara Falls, N. Y.; mailing address, Niagara Club.
NEUMANN, Wilhelm (Aug. 28, '14) Chemist, Gullspang Elektrokemiske, A. B., Gullspang, Sweden.
NEWMAN, P. J. (Apr. 22, '15) Asst. Prof. of Chem., Kansas State Agricultural College; mailing address, 914 Leavenworth St., Manhattan, Kansas.
NICHOLS, Wm. H., D.Sc., LL.D. (Mar. 3, '06) Pres., Nichols Copper Co., General Chem. Co., 25 Broad St., New York; res., 355 Clinton Ave., Brooklyn, N. Y.
NICHOLS, W. Standish (Apr. 3, '02) Consulting Engineer, 100 Broadway, New York City.
NICKERSON, William E. (May 29, '09) Consulting Mechanical Engineer, Gillette Safety Razor Co., So. Boston, Mass.; mailing address, 1722 Massachusetts Ave., Cambridge, Mass.
NISHIKAWA, Kikei (Jan. 29, '10) 8 Kaguraoka, Yoshida St., Kyoto, Japan.
NISWONGER, E. E. (Apr. 29, '11) President, The National Laundry Machinery Co., 731 W. Third St., Dayton, O.
NOGUCHI, Jun (Apr. 24, '14) Tosabori-uramachi, Nishiku, Osaka, Japan.
NOHARA, Dr. Tsuneo (Apr. 6, '11) Engr., 2, Iida-machi 4 Chome, Kojimachi-Ku, Tokyo, Japan.

NORMAN, Geo. M. (Apr. 3, '02) Hercules Powder Co., Wilmington, Del.
NORTHRUP, Edwin F. (Oct. 17, '07) Palmer Physical Laboratory, Princeton, N. J.
NOYES, Harry L. (Feb. 25, '16) Chief Eng., Union Carbide Co., Niagara Falls, N. Y.
NUTTING, E. G. (Dec. 30, '16) Chemist, The Carborundum Co.; mailing address, 1511 Pine Ave., No. 6, Niagara Falls, N. Y.
OAKDEN, William E. (Oct. 29, '10) 11 Lonsdale Road, Barnes, London, S. W., England.
OBER, Julius E. (Apr. 24, '09) c/o West Penn Steel Co., Brackenridge, Pa.
OFFUTT, John W. (June 27, '13) Supt., Shelby Steel Co., Ellwood City, Pa.
OGDEN, John (Sept. 27, '16) Mgr., Ogden Laboratories, 230 Chancellor St., Philadelphia, Pa.
OHLWILER, Clarence H. (Apr. 6, '11) Chemist, Aetna Chem. Co., 303 Reamer Ave., Carnegie, Pa.
OLAUSSON, K. O. Ernfrid (Oct. 28, '09) Electrometallurgical Engineer, Aktiebolaget Saxberget, Trollhättan, Sweden.
OLDRIGHT, G. L. (June 30, '16) Shift Supt., Leaching Plant, c/o Chile Exploration Co., Via Antofagasta, Chuquicamata, Chile.
OLSEN, Hjalmar (Nov. 26, '10) Chief Chemist, N. Western Cyanamid Co., Ltd., Bygdo alle No. 1, Kristiana, Norway.
OLSEN, T. S. (Nov. 26, '15) Det Norske A/S for Electrokemisk Industri, Bygdo Alle III, Kristiana, Norway.
OLSON, Carl G. (Aug. 25, '16) Chief Eng., Illinois Tool Works; mailing address, 154 E. Erie St., Chicago, Ill.
OLSSON, Henning (July 26, '12) Chief Designer, Hertzia, Gottenborg, Sweden.
ORDWAY, Daniel L. (May 5, '10) Asst. Director, Research Laboratory, National Carbon Co., Cleveland, Ohio; res., 1428 Ridgewood Ave., Lakewood, Ohio.
ORNSTEIN, Geo., Ph.D. (May 29, '09) Electrochemist, Tech. Mgr., Electro Bleaching Gas Co., and Niagara Alkali Co., 18 E. 41st St., New York City.
ORR, Chester A. (Jan. 28, '16) Mgr., The Cleveland Metal Products Co., Cleveland, Ohio.
OSBORNE, Loyall A. (Apr. 3, '02) Westinghouse E. and Mfg. Co., Pittsburgh, Pa.
OSBORNE, Sidney E. (Jan. 28, '16) Asst. Eng., Hooker Electrochemical Co.; mailing address, 170 Buffalo Ave., Niagara Falls, N. Y.
OSHIMA, Yoshikiyo, Dr. Ing. (July 30, '09) Graduate College Bldg., Princeton University, Princeton, N. J.
OSTHEIMER, John W. (June 25, '09) Ingenieur des Arts and Manufactures, 3 rue Rabelais, Paris, France.
PAGE, George S. (May 29, '09) Asst. Mgr., Park Works, Crucible Steel Co. of America, Pittsburgh, Pa.
PAGE, Wm. K. (Feb. 21, '13) c/o Chile Exploration Co., Chuquicamata, Chile.
PALMER, Wm. R. (May 29, '09) General Supt., American Tube & Stamping Co., Bridgeport, Conn.; mailing address, 827 Seavind Ave.
PARISH, Ralph R. (Oct. 24, '13) Rome Brass & Copper Co., Rome, N. Y.
PARKER, James H. (Nov. 26, '10) Metallurgist, Carpenter Steel Co., Reading, Pa.; res., 109 Windsor St.
PARKHURST, C. W. (Sept. 26, '08) Supt. El. Dept., Cambria Steel Co., Johnstown, Pa.
PARKHURST, I. P. (Oct. 21, '16) Instructor of Chem., Univ. of Kansas, Lawrence, Kansas.
PARKINSON, J. Carl (Feb. 25, '11) 704 Third Ave., Tarentum, Pa.
PARKS, R. E. (May 22, '14) c/o Aluminum Co. of America, Maryville, Tenn.
PARMELEE, Howard C. (June 28, '12) Pres., Colo. School of Mines, Golden, Colo.
PARR, Samuel W. (Jan. 7, '05) Prof. of Applied Chem., Univ. of Ill., Urbana, Ill.
PARSONS, Charles L. (Oct. 29, '08) Prof. of Inorganic Chemistry, Box 505, Washington, D. C.
PARSONS, Louis A., Ph. D. (Apr. 3, '02) Prof. of Physics, Pennsylvania College, Gettysburg, Pa.
PASCOE C. F. (Nov. 24, '11) Metallurgist, c/o Thos. Davidson Mfg. Co. Ltd., Montreal, Canada.
PATCH, N. K. B. (Jan. 23, '14) Factory Engineer, Lumen Bearing Co., Buffalo, N. Y.
PATRICK, Ralph C. (Sept. 27, '16) Chem. Eng., Wolverine Brass Works, Grand Rapids, Mich.; mailing address, 1315 Scribner Ave., N. W.
PATTEN, Harrison E., Ph.D. (Sept 15, '07) Bureau of Chemistry, Washington, D. C.
PATTERSON, T. A. (Sept. 27, '16) Supt., Elizabeth Plant, Morris Herrmann & Co., 3d and Trumbull Sts., Elizabeth, N. J.
PATTON, D. C. (Oct. 22, '15) Works Representative, Tolhurst Machine Works, Troy, N. Y.
PAUL, Henry N. Jr., (Apr. 3, '02) 1815 Land Title Bldg., Philadelphia, Pa.
PEARCE, J. Newton (Apr. 29, '11) Assistant Professor of Chemistry, The State University of Iowa, Iowa City, Iowa; res., 714 Iowa Ave.
PECK, Eugene C. (May 5, '10) Gen. Supt., The Cleveland Twist Drill Co., Cleveland, Ohio; res., 6719 Euclid Ave.
PEDDER, John (Apr. 27, '12) Chemist, West Virginia Pulp & Paper Co., Luke, Md.

PEDERSEN, Arthur Z. (Aug. 25, '16) Chemist, Edison Storage Battery Co., 86 Mt. Pleasant Ave., West Orange, N. J.
PEILER, Karl E. (Apr. 27, '12) Mech. Engineer, W. A. Lorenz, Hartford, Conn.; res., 56 Allen Place, Hartford, Conn.
PEIRCE, Wm. H. (Apr. 6, '11) Vice-President and General Mgr., Baltimore Copper Smelt. and Roll. Co., P. O. Station J, Baltimore, Md.
PENNIE, John C. (May 29, '09) Attorney at Law and Patent Solicitor, 35 Nassau St., New York City.
PENNOCK, John D., A.B. (Apr. 2, '04) Chief Chemist, Solvay Process Co., Syracuse, N. Y.
PERLEY, Geo. A. (Apr. 26, '13) Asst. Prof. of Physical Chemistry, N. H. College, Durham, N. H.
PERRY, C. M. (Sept. 4, '03) Greene, Rhode Island.
PETERS, Frazier F. (Oct. 21, '16) The Dorr Co., 227 West 90th St., New York City.
PETERSON, Andrew P. (Oct. 29, '10) Western Electric Co., 1515 W. Monroe St., Chicago, Ill.
PETINOT, Napoleon (Apr. 24, '09) Electrometallurgical Engr., 25 Claremont Ave., New York City.
PETTEE, C. L. W. (Aug. 25, '16) Owner and Mgr., The Hartford Laboratory Co., P. O. Drawer 9, Hartford, Conn.
PFANSTIEHL, Carl (Sept. 27, '16) Pres. Pfanstiehl Co., Wood Path, Highland Park, Ill.
PHILLIP, Herbert (Nov. 6, '03) Roessler & Hasslacher Chem. Co.; res., 152 High St., Perth Amboy, N. J.
PHILLIPS, Ross (Nov. 6, '03) National Electrolytic Co., Niagara Falls, N. Y.
PICKENS, Rufus H. (Jan. 27, '12) Southern Public Utilities Co., Clemmons, N. C.
PICKERING, Oscar W. (Oct. 2, '02) 76 Bennett Ave., Arlington, N. J.
PIKLER, A. Henry (June 1, '07) Üllör-ut 30, Budapest, Hungary.
PINKERTON, Andrew (Apr. 3, '03) Box 427, Pittsburgh, Pa.
PLEISS, Paul (Nov. 28, '13) 1401 Jackson Boulevard, Chicago, Ill.
POMEROY, R. E. H. (Sept. 27, '16) Supt. of Smelt. Dept., Nevada Consol. Copper Co.; mailing address, P. O. Box 612, McGill, Nevada.
POND, G. G., Ph. D. (July 3, '02) Prof. of Chem., State College, Pa.
POPE, Chas. E. (Feb. 25, '11) President, Coal and Coke By-Products Co., 421 Wood St., Pittsburgh, Pa.
POPE, Ralph W. (Apr. 26, '16) Sec'y and Treas., Aluminum Plated Ware Co., 397 Market St., Newark, N. J.
PRATT, E. Bruce (Dec. 26, '13) Agent, Mutual Benefit Life Insurance Co.; mailing address, 908-16 Hippodrome Bldg., Cleveland, Ohio.
PRATT, Fred. S. (Apr. 3, '02) Stone & Webster, 147 Milk St., Boston, Mass.
PRATT, H. A. (Sept. 27, '16) Mgr., Industrial Div., N. Y. Office, Westinghouse Elec. & Mfg. Co.; mailing address, 138 Debacy Ave., N. Plainfield, N. J.
PRICE, Edgar F. (July 3, '02) 42d St. Bldg., Cor. 42d St. and Madison Ave., New York City.
PRICE, Wm. B. (Mar. 27, '14) Chief Chemist, Scovill Mfg. Co.; mailing address, 111 Euclid Ave., Waterbury, Conn.
PRINDLE, Edwin J. (Jan. 8, '04) Prindle, Wright & Small, Patent Lawyers, The Trinity Bldg., 111 Broadway, New York City.
PRING, John N. (Nov. 3, '06) Lecturer on Electrochem., Victoria Univ., Manchester, England.
PRITZ, L. G. (Oct. 23, '14) Supt. of Special Steels, c/o Illinois Steel Co., So. Chicago, Ill.
PRITZ, Wesley B. (May 5, '10) Asst. Supt., c/o The American Carbon & Battery Co., East St. Louis, Ill.
PROCTOR, Chas. H. (Apr. 29, '11) Supervisor in Plating and Finishing Dept., F. H. Lovell & Co., Arlington, N. J.; res., 270 Argyle Place.
PROSSER, H. A. (Dec. 2, '05) Director and Member of Executive Com., American Smelt. and Ref. Co., 120 Broadway, New York City.
PULMAN, Oscar S. (May 26, '10) Asst. Superintendent, National Carbon Co., Cleveland, Ohio; res., 1507 Cohasset Ave., Lakewood, Ohio.
PULSIFER, H. B. (Nov. 24, '16) Asst. Prof. of Met., Armour Inst. of Tech., Chicago, Ill.
PUTNAM, Wm. R. (Oct. 21, '16) Sales Mgr., Utah Power & Light Co., 515 Keams Bldg., Salt Lake City, Utah.
PYNE, Francis R. (Dec. 2, '05) U. S. Metals Ref. Co., Chrome, N. J.; res., 29 Scotland Road, Elizabeth, N. J.
QUEENY, John F. (June 1. '07) President, Monsanto Chem. Co., 1800 S. 2d St., St. Louis, Mo.
QUENEAU, A. L. J. (May 1, '06) Jemeppe s/Meuse, Belgium.
QUINAN, Kenneth B. (Jan. 8, '04) Chief Chemist, De Beer's Explosive Works, Dynamite Factory, Somerset West, Cape Colony, Africa.
RAEDER, Bjorn (Jan. 23, '14) Chief of Experimental Dept. Comp. de Meteaux, Overpelt-Lammel, Neerpelt, Belgium.
RAETH, Frederick C. (Dec. 29, '11) Teacher of Electrochemistry, School of Practical Electricity, Stroh Bldg., Milwaukee, Wis.
RALSTON, Oliver C. (July 23, '15) Asst. Met., U. S. Bureau of Mines, c/o University of Utah, Salt Lake City, Utah.

RAMAGE, A. S. (May 6, '05) International Color and Chemical Co., Inc., 435 Guoin St., Detroit, Mich.
RAMSEY, F. H. (Jan. 23, '14) Babcock & Wilcox Co., Bayonne, N. J.
RANDALL, A. G. (Sept. 27, '16) Gen. Foreman, Betts Plant, American Smelting and Ref. Co.; mailing address, 4256 Wirt St., Omaha, Neb.
RANDALL, J. W. H. (Jan. 29, '09) Chem. Eng., West Va. Pulp & Paper Co., Piedmont, W. Va.
RANDALL, Merle (Nov. 27, '09) Res. Associate, Chemistry Bldg., Univ. of Cal., Berkeley, Cal.
RANDOLPH, C. P. (Mar. 23, '12) 9 Elizabeth St., Pittsfield, Mass.
RANDOLPH, Edward (Feb. 27, '09) President, Balbach Smelting and Refining Co., Bretton Hall, New York City.
RANKIN, Herbert E. (Nov. 24, '11) Cherry Hill, Albany, N. Y.
RAUTH, John W. (Sept. 27, '16) Prof. of Chem., Mt. St. Mary's College, Emmitsburg, Md.
RAY, Horatio C. (June 27, '13) Prof. of Ore Dressing & Assoc. Prof. of Metallurgy, School of Mines, Univ. of Pittsburgh, Pa.
REBER, Col. Samuel, U. S. A. (Apr. 3, '02) Federal Bldg., Chicago, Ill.
REDFIELD, C. S. (Apr. 26, '16) Chief Chem., Empire Rubber & Tire Co., Box 502, Trenton, N. J.
REED, Avery H. (Apr. 6, '11) Supt. of Mines, Rosiclare Lead and Fluorspar Mines, Marion, Ky.
REED, C. J. (Apr. 3, '02) 507 Brannan St., San Francisco, Cal.
REED, John C. (Apr. 29, '11) Electrical Engr., Bethlehem Steel Co., Steelton, Pa.
REED, S. Albert (June 1, '15) 113 E. 55th St., New York City.
REESE, P. P. (May 29, '09) Metallurgist, 125 12th St., N. W., Canton, Ohio.
REEVE, Amos G. (Nov. 26, '07) Electroplating Dept., Oneida Community, Ltd., Kenwood, N. Y.
REEVE, H. T. (Mar. 24, '16) Chief Scientist, American Optical Co., Southbridge, Mass.
REICH, J. S. (Aug. 25, '16) Asst. Supt. and Chemist, Harrison Chemical Co.; mailing address, 681 Lincoln Place, Brooklyn, N. Y.
REID, John T. (Mar. 27, '09) Mining Engineer, Nevada Mining Co., Lovelock, Humboldt Co., Nev.
REINBOLD, Dr. Herman (Oct. 21, '16) Pres., Reinbold Met. & Potash Products Co., 712 Omaha National Bank Bldg., Omaha, Neb.
REISENEGGER, Dr. Herman (June 6, '03) Charlottenburg technische Hochschule, 172 Berliner St., Charlottenburg, Germany.
REIST, Henry G. (Sept. 26, '08) Desig. Eng., Gen. El. Co., Schenectady, N. Y.
RESE, Wm. F. (July 24, '14) Electrician, c/o Weirton Steel Co., Weirton, W. Va.
RHODIN, B. E. F. (Nov. 26, '15) c/o The Hooker Electrochemical Co., Niagara Falls, N. Y.
RICH, William J. (May 26, '10) Principal Examiner, U. S. Patent Office, Room 175, Washington, D. C.
RICHARDS, Edgar (Feb. 27, '09) 60 Ayrault St., Newport, R. I.
RICHARDS, Jos. W., Ph. D. (Apr. 3, '02) Prof. of Metallurgy, Lehigh Univ., S. Bethlehem, Pa.; res., University Park.
RICHARDS, Percy J. (Nov. 24, '16) Chemist, with J. W. Richards, Assayer and Chemist, 1118 19th St., Denver, Colo.
RICHARDS, Dr. T. W. (June 3, '05) Prof. of Chem., W. Gibbs Mem. Lab., Harvard Univ., Cambridge, Mass.
RICHARDSON, C. N. (Dec. 30, '16) Electrochemist, Titanium Alloy Mfg. Co.; mailing address, 722 Park Place, Niagara Falls, N. Y.
RICHARDSON, E. A. (Apr. 6, '11) Chemist, Euclid Glass Division, General Electric Co., E. 152 St., Cleveland, Ohio.
RICHARDSON, E. H. (Sept. 27, '16) Secretary, Hotpoint Electric Heating Co., Ontario, Cal.
RICHARDSON, Henry K. (May 29, '09) 105 Clowes Terrace, Waterbury, Conn.
RICHARDSON, L. T. (Apr. 6, '11) Chem. Eng., c/o The Cutler-Hammer Mfg. Co., Milwaukee, Wis.
RICHARDSON, W. D. (Sept. 24, '10) Chief Chemist and Chem. Eng., Swift & Co., Chicago, Ill.; res., 4215 Prairie Ave.
RICHTER, Geo. A. (Feb. 25, '16) Res. Chem. Eng., Research Lab., Berlin Mills Co., Berlin, N. H.
RICKETTS, Louis D. (Apr. 24, '14) Consulting Engineer, 42 Broadway, New York City.
RIGLANDER, Moses M. (Apr. 6, '11) President, Multiple Unit Electric Co., New York City; mailing address, 47 Maiden Lane.
RIKER, John J. (Mar. 5, '03) Treas., Oldbury Electrochem. Co., 19 Cedar St., New York City.
RILEY, L. A., 2d (Aug. 25, '16) Practicing Eng., 52 Vanderbilt Ave., New York City.
RIPPEL, Ernest G. (Oct. 23, '14) Consult. Met., Buffalo Foundry and Machine Co., 941 West Ave., Buffalo, N. Y.
RITTENHOUSE, Edward (Aug. 25, '16) Chemist, The Viscose Co., Marcus Hook, Pa.
RITTER, Burr H. (Nov. 26, '15) Chemist, Hooker Electrochemical Co.; mailing address, 251 Third St., Niagara Falls, N. Y.

ROBB, Chas. D. (Nov. 27, '09) Essex Falls, New Jersey.
ROBERTS, Isaiah L. (Oct. 2, '02) Nueva Gerona, Isle of Pines, Cuba.
ROBINSON, Almon (Apr. 3, '02) Webster Road, Lewiston, Me.
ROBINSON, Frederic W. (May 25, '12) Chemist, The Hanovia Chem. & Mfg. Co., Newark, N. J.; res., 1011 Broad St.
RODMAN, Hugh (Apr. 3, '02) c/o Rodman Chem. Co., E. Pittsburgh, Pa.
ROEBER, E. F., Ph.D. (Apr. 3, '02) Editor, Metallurgical and Chemical Engineering, 239 W. 39th St., New York City.
ROESSLER, E. B. (Sept. 27, '16) Student in Chem. Engineering, Univ. of Cincinnati; mailing address, 3459 Brookline Ave.
ROESSLER, Dr. Franz (July 31, '07) Vice-Pres. and Supt., Roessler & Hasslacher Chem. Co., Perth Amboy, N. J.; res., 39 High St.
ROLLER, F. W. (Apr. 3, '02) Elec. Instruments (Machado & Roller), 203 Broadway, New York City.
ROLL-HANSEN, Cay (Sept. 27, '16) Supt. Keokuk Electro Metals Co., Keokuk, Iowa; mailing address, 317 Concert St.
ROLLIN, Hugh (Mar. 24, '16) Pres., Rollin Chem. Co., Inc., Charleston, W. Va.
ROMANELLI, Emilio (Jan. 28, '11) 21 Willard Ave., Bloomfield, N. J.
ROSENGARTEN, Geo. D. (Apr. 29, '11) Vice-President, Powers-Weightman-Rosengarten Co., P. O. Box 1625, Philadelphia; res., Malvern, Pa.
ROSS, Bennett B. (Feb. 27, '14) Auburn, Ala.
ROSSI, A. J. (Apr. 3, '02) 35 Broadway, New York City.
ROSSI, Dottor Carlo (Mar. 23, '12) Legnano, (Milan) Italy.
ROSSI, Louis M. (Jan. 29, '10) Chemist, Wks. Mgr., General Bakelite Co., New York City; res., 135 Rector St., Perth Amboy, N. J.
ROTH, Charles F. (Oct. 22, '15) Consult. Chemist, Industrial Filtration Corp., 115 Broadway, New York City; mailing address, 609 West 178th St.
ROUSE, Edwin W., Jr. (Feb. 27, '09) Asst. Supt., Baltimore Copper Smelting and Rolling Co., Baltimore, Md.
ROUSH, G. A. (Feb. 6, '04) Asst. Prof., Dept. of Metallurgy, Lehigh University, Editor of "Mineral Industry," South Bethlehem, Pa.
ROWAND, Lewis G. (April 3, '02) c/o New Jersey Zinc Co., 55 Wall St., New York City.
ROWELL, J. C. (Jan. 25, '13) Librarian, University Library, Berkeley, Cal.
ROWLAND, J. M. (Nov. 26, '15) Construction Eng., Hooker Electrochemical Co.; mailing address, 531 Buffalo Ave., Niagara Falls, N. Y.
ROWLANDS, Thos. (Feb. 27, '09) Windsor Works, North Church St., Sheffield, England.
RUEL, Amai J .(Mar. 26, '15) Chief Engineer and Supt., No. Idaho & Montana Power Co., Sandpoint, Idaho.
RUHL, Louis (Dec. 2, '05) Asst. Sec., The Roessler & Hasslacher Chem. Co., 100 William St., P. O. Box 1999, New York City.
RUHOFF, O. E. (Oct. 21, '16) Eng., French Battery & Carbon Co., Madison, Wis.
RUPPEL, Henry E. K. (May 29, '09) Chemist, 66 Willow St., Wollaston, Mass.
RUSHMORE, D. B. (Oct. 2, '02) Eng. Power & Min Dept., General Electric Co., Schenectady, N. Y.
RUSSELL, Chas. J. (Apr. 3, '02) District Manager, The Phila. Electric Co., 4522 Frankford Ave., Philadelphia, Pa.
RUSSELL, Christopher A. (May 27, '11) Star Electric Co., Niagara Falls, N. Y.
RUTHENBURG, Marcus (Apr. 3, '02) Met. Eng., 4 Southampton Row, Holborn, London, W. C., England.
RYAN, Harris J. (Nov. 30, '12) Prof. of Electrical Engineering, Leland Stanford Univ., Stanford Univ. P. O., California.
RYPINSKI, M. C. (June 30, '16) Mgr., Meter and Transformer Dept., Westinghouse Electric and Mfg. Co., Pittsburgh, Pa.; mailing address, 702 Hastings St.
SADTLER, Samuel P., LL.D. (Apr. 3, '02) Consulting Chemist, S. P. Sadtler & Son, 210 S. 13th St., Philadelphia, Pa.
SADTLER, Samuel S. (Apr. 3, '02) with S. P. Sadtler & Son, Consulting and Analytical Chemists, 210 S. 13th St., Philadelphia, Pa.
SAKLATWALLA, B. D. (May 26, '10) General Superintendent, American Vanadium Co., Bridgeville, Pa.; res., 47 McMunn Ave., Crofton, Pa.
SALOM, Pedro G. (Apr. 3, '02) Commonwealth Trust Bldg., 12th and Chestnut Sts., Philadelphia, Pa.
SAMUELS, Wm. P. (May 5, '10) 120 Smithfield St., New Castle, Pa.
SARGENT, Frank C. (Jan. 29, '09) 201 Devonshire St., Boston, Mass.
SARGENT, Geo. W. (Apr. 29, '11) Metallurgist and Chemist, Crucible Steel Co. of America, Oliver Bldg., Pittsburgh, Pa.
SARGENT, R. N. (Oct. 27, '11) Works Mgr., Plant C. E., Roessler & Hasslacher Chem. Co., St. Albans, W. Va.; res., 153 State St., Perth Amboy, N. J.
SAUNDERS, Prof. A. P. (Apr. 3, '02) Hamilton College, Clinton, N. Y.
SAUNDERS, Lewis E. (Dec. 26, '07) Mgr., Abrasive Plants, Norton Co., 114 Buffalo Ave., Niagara Falls, N. Y.
SAUNDERS, Walter M. (Mar. 27, '09) Saunders & Franklin, Providence, R. I.; mailing address, 20 Dewey St.
SCHALL, Dr. C. (Aug. 29, '08) Prof. of Chemistry, Solomonstr. 1, Leipzig, Germany.
SCHAMBERG, Meyer (Dec. 27, '07) Chemist and Min. Engr., 1841 N. 17th St., Philadelphia, Pa.

SCHAPIRO, H. (Oct. 22, '15) Chief Chemist, The Ohio Match Co., Wadsworth, Ohio.
SCHILDHAUER, Edward (Dec. 26, '08) El. and Mech. Eng., c/o The Engineers Club, 32 W. 40th St., New York City.
SCHLEEDER, L. Bertram (Apr. 29, '11) Chemist, Dr. F. J. Maywald, 89 Pine St., New York City; res., 130 N. Penn St., York Pa.
SCHLOSS, Joseph A. (Jan. 29, '09) Ore Buyer, 42 Broadway, New York City.
SCHLUEDERBERG, Carl G. (Feb. 2, '06) Asst. to Mgr., Supply Dept., Westinghouse El. & Mfg. Co., East Pittsburgh, Pa.; 210 N. Craig St., Pittsburgh, Pa.
SCHLUNDT, Herman (Nov. 5, '04) Prof. of Physical Chemistry, University of Missouri, Columbia, Mo.; res., 303 Hicks Ave.
SCHMELZ, Ernest M. (July 24, '14) Consult. Eng., 611 Moffat Bldg., Detroit, Mich.
SCHOCH, Dr. Eugene P. (Oct. 1, '04) Prof. of Chem., Univ. of Texas; res., 2212 Nucces St., Austin, Texas.
SCHOELLKOPF, Jacob F., Jr. (Dec. 31, '15) Chemist, P. O. Drawer 57, Buffalo, N. Y.
SCHOELLKOPF, Paul A. (Dec. 31, '15) Gen. Mgr., Hydraulic Power Co., Niagara Falls, N. Y.
SCHOEPF, T. H. (June 30, '16) c/o Westinghouse Electric & Mfg. Co., East Pittsburgh, Pa.
SCHRAMM, Edward (Oct. 21, '16) Asst. Chemist, Bureau of Standards, 16 W. Kirke St., Chevy Chase, Md.
SCHREY, Adolf (Nov. 26, '10) Sidonianstrasse 10, Dresden A, Germany.
SCHROEDER, C. M. Edward (May 29, '09) Chief Assistant, Standard Bleaching Co., Carlton Hill, N. J.; mailing address, 235 Wood St., Rutherford, N. J.
SCHUBERT, Bruno H. (Aug. 25, '16) Inspector and Chemist, R. W. Hunt & Co.; mailing address, 224 Jane St., Weehawken, N. J.
SCHUELER, J. L. (Sept. 27, '16) Chemist and Met., Keystone Steel and Wire Co., Peoria, Ill.
SCHUETZ, Fred. F. (Oct. 1, '04) Patent Attorney, Room 1352, 50 Church St., New York City.
SCHULTE, Walter B. (Oct. 29, '10) Treasurer, C. F. Burgess Laboratories, 625 Williamson St., Madison, Wis.
SCHULTZ, Louis Claude (Oct. 22, '15) Chem. Eng., c/o Hamilton & Hansell, 17 Battery Place, New York City.
SCHUYLER, A. H. (June 2, '16) Metallurgist, International Nickel Co., Bayonne, N. J.
SCHWARTZ, T. L. (July 28, '16) Mgr., Supply Division, Westinghouse Electric and Mfg. Co., 780 Ellicott Square, Buffalo, N. Y.
SCHWARZ, Ralph C. (May 5, '10) Electrical Engineer, Taylor Instrument Co., Rochester, N. Y.
SCOTT, Arthur P. (Mar. 27, '09) Metallurgist, c/o American Smelt. and Ref. Co., National Place, So. Chicago, Ill.
SCOTT, Professor Chas. F. (Aug. 27, '09) 284 Orange St., New Haven, Conn.
SCOTT, L. C. (Oct. 21, '16) Res. Chem. Eng., Aluminum Co. of America; mailing address, Box 211, Massena, N. Y.
SCUDDER, Heyward (Sept. 4, '03) 107 E. 34th St., New York City.
SEEDE, John A. (May 29, '09) Elec. Eng., General Electric Co., Schenectady, N. Y.; mailing address, Route 49, Schenectady, N. Y.
SEGUINE, Wm. (Nov. 28, '13) Res. Lab., Grasselli Chem Co., Cleveland, Ohio.
SERGEANT, Elliott M. (October 1, '04) Box 54, Niagara Falls, N. Y.
SESSIONS, R. L. (Feb. 27, '14) Chem. Engineer, Vanadium Alloys Steel Co., Latrobe, Pa.
SETHMAN, Geo. H. (Nov. 6, '03) Engineer and Constructor, Suite 250, Equitable Bldg., Denver, Colo.
SEWARD, Geo. O. (April 3, '02) 99 Cedar St., New York City.
SEYFERT, Stanley S. (Oct. 29, '08) Assoc. Prof., El. Eng., Lehigh Univ.; res. 456 Chestnut Street, South Bethlehem, Pa.
SHARP, Clayton H., Ph.D. (Nov. 26, '07) Technical Director, Electrical Testing Laboratories, 80th St. and East End Ave., New York City; res., White Plains, New York.
SHARPLES, Stephen P. (Feb. 27, '09) Consulting Chemist, Campbell Magnetic Separator Co., Boston, Mass.; mailing address, 26 Broad St.
SHATTUCK, A. F. (Apr. 3, '02) The Solvay Process Co., Detroit, Mich.
SHAW, E. C. (Apr. 3, '02) North Portage Path, Akron, Ohio.
SHELDON, Dr. Samuel (Apr. 3, '02) Prof. of Physics and Elec. Eng., Polytechnic Inst., Brooklyn, N. Y.
SHEPHERD, F. A. (Nov. 27, '14) Electroplating Eng., International Steel and Ordnance Co., Lowell, Mass.
SHEPHERD, F. R. (Sept. 25, '14) Chief Electrical Inspector, P. O. Box 361, Dunedin, N. Z.
SHIELDS, Dr. John (Dec. 4, '02) Minas de Rio Tinto, Provincia de Huelva, Spain.
SHIMER, Edward B. (Jan. 28, '11) Asst., Porter W. Shimer Laboratory, Paxinosa Ave., Easton, Pa.
SHIVERICK, Myron D. (Nov. 21, '08) 25 Menands Road, Menands, N. Y.
SHOAFF, P. S. (Sept. 27, '16) Chem. Eng., Sea Products Co. & Oceanic Eng. Corp.; mailing address, 421 Daisy Ave., Long Beach, Cal.

SIEGER, Geo. N. (Apr. 27, '12) Asst. to Mgr., Electrolytic Dept., Davis-Bournonville Co., Marion Station, Jersey City, N. J.
SIEVERING, Philip (Apr. 26, '13) Electroplater, Philip Sievering Co., 54 Nairn Place, Newark, N. J.
SILVERMAN, R. B. (Mar. 27, '14) Chief Chemist, Hydrometallurgist, c/o Butte-Duluth Mining Co., Butte, Mont.; mailing address, 406 E. Missouri St., El Paso, Texas.
SIMMERS, Arthur L. (May 29, '09) Eng., P. O. Box 791, Niagara Falls, N. Y.
SIMPSON, Louis (May 29, '09) 172 O'Connor St., Ottawa, Canada.
SIMS, C. E. (June 1, '15) Anaconda Copper Co., General Delivery, Anaconda, Mont.
SKILLMAN, Verne (Mar. 26, '10) care of Lumen Bearing Co., Buffalo, New York.
SKINNER, Chas. E. (Dec. 31, '09) Engineer, Research Division, Westinghouse Elec. and Mfg. Co., Wilkinsburg, Pa.; mailing address, 1309 Singer Place.
SKINNER, H. J. (Apr. 3, '02) The State College of Washington, Pullman, Wash.
SKINNER, L. B. (Oct. 23, '14) V. P. and Gen. Mgr., Western Chem. Mfg. Co., Denver, Colo.
SKOWRONSKI, Stanislaus (June 1, '07) care of Raritan Copper Works, Perth Amboy, New Jersey.
SLADE, W. C. (Apr. 30, '08) Supt. of Power and Lines, Rhode Island Co., Providence, R. I.; mailing address, 83 Grotto Ave.
SLATER, Wm. A. (Feb. 25, '11) Chemist, Gulf Refining Co., P. O. Box 1024, Ft. Worth, Texas.
SLOCUM, Frank L., Ph.D. (Dec. 4, '03) Chem. Eng., c/o Mackintosh, Hemphill & Co., 401 S. Linden Ave., E. E., Pittsburgh, Pa.
SMITH, Acheson (Aug. 31, '07) Vice-Pres. and Gen. Mgr., Inter. Acheson Graphite Co.; res., 113 Jefferson Ave., Niagara Falls, N. Y.
SMITH, A. T. (Dec. 4, '03) 257 Royal Liver Bldg., Liverpool, England.
SMITH, Prof. A. W. (Apr. 3, '02) 11333 Bellflower Road, Cleveland, Ohio.
SMITH, Dyer (June 28, '12) Patent Lawyer, 32 Liberty St., New York City; mailing address, 9 Wilde Place, Montclair, N. J.
SMITH, E. A. C. (May 9, '03) Consulting Engineer, 120 Broadway, New York City.
SMITH, Dr. Edgar F. (June 3, '05) Provost, Univ. of Penna., Philadelphia, Pa.
SMITH, Edmund S. (Apr. 3, '02) Chemist, The Carborundum Co., Niagara Falls, N. Y.
SMITH, E. W. (Apr. 3, '02) 74 E. Penn St., Germantown, Philadelphia, Pa.
SMITH, F. Warren (May 9, '03) Provo City, Utah.
SMITH, H. F., Jr. (Aug. 25, '16) Eng., E. W. Clark & Co., 321 Chestnut St., Philadelphia, Pa.
SMITH, Harold H. (Jan. 27, '12) Edison Storage Battery Co., Orange, N. J.
SMITH, Walter C. (Oct. 23, '14) Supt. Silver Bldg., U. S. Metals Ref. Co., Chrome, N. J.
SMULL, Judson G. (Nov. 26, '07) National Lead Co., 617 Stoolhoff Ave., Richmond Hill, Long Island, N. Y.
SMYTHE, Edwin H. (May 29, '09) Electrical Engineer, 738 Monadnock Bldg., Chicago, Ill.
SNEATH, Wm. H. (May 25, '12) Asst. Supt., Electro Metallurgical Co., La Salle, N. Y.
SNOOK, H. Clyde, A.M. (Nov. 26, '07) 224 Linden Ave., Oak Park, Ill.
SNOW, Wm. M. (Feb. 25, '11) Supt. of Acid Works, Illinois Zinc Co., Peru, Ill.
SNOWDEN, R. C. (Feb. 3, '06) Operation Expert, Hooker Electrochemical Co.; mailing address, 21 C St., Niagara Falls, N. Y.
SNYDER, Fred. T. (June 6, '03) Snyder Electric Furnace Co., 738 Monadnock Bldg., Chicago, Ill.
SNYDER, J. L. K. (May 5, '10) Supt., Howard Plants, Aetna Explosives Co., Inc., Emporium, Pa.
SODERBERG, Carl W. (Oct. 29, '10) Det norske Aktieselskap for Elektrokemiske Industri, Christiania, Norway.
SOLVAY, Armand (Jan. 8, '04) Mgr., The Solvay Co. of Brussels, 33 rue du Prince Albert, Brussels, Belgium.
SOMDAL, John A. (Jan. 22, 1915), Res. Chemist, The Aluminum Co. of America, Massena, N. Y.
SPARRE, Fin, Dr. (Oct. 26, '12) 606 W. 20th St., Wilmington, Delaware; mailing address, Director, care of Experimental Station, E. I. du Pont de Nemours & Co., Henry Clay P. O., Delaware.
SPEED, Buckner (Dec. 31, '14) Head of Physical Lab., Western Electric Co.; mailing address, 463 West St., New York City.
SPEIDEN, Clement C. (Nov. 6, '02) 46 Cliff St., New York City.
SPEIDEN, Eben C. (Feb. 2, '06) Vice-Pres. and Gen. Mgr., c/o Isco Chem. Co., Inc., Niagara Falls, N. Y.
SPELLER, Frank N. (Jan. 29, '10) Met. Eng., National Tube Co., 1824 Frick Bldg., Pittsburgh, Pa.; res., 1624 Wightman St.
SPENCER, A. G. (Sept. 27, '16) Chief Chemist and Dir. of Test Dept., c/o Canadian Inspection and Test. Labs. Ltd., 601-611 Canadian Express Bldg., Montreal, Canada.
SPERRY, Elmer A. (Apr. 3, '02) 100 Marlborough Road, Prospect Park, South, Brooklyn, N. Y.
SPERRY, R. S. (June 1, '15) Res. Eng., Scovill Mfg. Co., Waterbury, Conn.

SPICER, C. W. (Aug. 25, '16) Vice-Pres. and Chief Eng., Spicer Mfg. Co., Plainfield, N. J.
SPILSBURY, Edmund G. (Jan. 28, '11) Consulting Min. Engr., 45 Broadway, New York City.
SPRAGUE, Edmund C. (July 31, '08) Chemist, c/o E. G. Acheson, Ltd., 5 Chancery Lane, London, W. C., England.
STAFFORD, Samuel G. (May 26, '10) Vice-Pres. and Gen Mgr., Vulcan Crucible Steel Co., Aliquippa, Pa.; res., State St., Coraopolis, Pa.
STAHL, Nicholas (Aug. 25, '16) Commercial Eng., Westinghouse El. & Mfg. Co.; mailing address, 204 Hawthorn St., Swissvale Station, Pittsburgh, Pa.
STAMPS, F. A. (June 2, '06) Chem., c/o Phosphorus Compounds Co., Niagara Falls, N. Y.
STANSFIELD, A., D.Sc., A.R.S.M. (Jan. 8, '03) Prof. of Metallurgy, McGill Univ., Montreal, Canada.
STARK, Edgar E. (Jan. 29, '09) City Electrician, Box 526, Christ Church, New Zealand.
STARR, Arthur B., Jr. (Feb. 25, '16) Power Salesman, Duquesne Light Co., 435 Sixth Ave., Pittsburgh, Pa.
STATHAM, Noel (Oct. 17, '07) Mgr. Chem. Dept., West Virginia Pulp & Paper Co., 200 5th Ave., New York City.
STEIN, Walter M. (Jan. 8, '03) Pres. and Gen. Mgr., Primos Chem. Co., Primos, Delaware Co., Pa.
STEINMETZ, Charles P. (Aug. 7, '02) Chief Consult. Eng., Gen. Elec. Co.; res., Wendell Ave., Schenectady, N. Y.
STEPHENS, Chas. E. (June 2, '16) Mgr., Illuminating Section, Supply Dept., Westinghouse Elec. & Mfg. Co.; mailing address, 1213 Center St., Wilkinsburg, Pa.
STEPHENSON, Frank T. F. (May 5, '10) Chemical Dept., Detroit Technical Institute, Detroit, Mich.; res., 873 Trumbull Ave., Detroit, Mich.
STEPHENSON, H. L. (July 28, '16) Salesman, Westinghouse Elec. & Mfg. Co., 780 Ellicott Square, Buffalo, N. Y.
STEVENS, J. Franklin (Sept. 26, '08) Engr., 1326 Chestnut St., Philadelphia, Pa.
STEVENS, W. L. (Sept. 15, '15) Metallurgical Accountant, Braden Copper Co., Rancagua, Chile.
STEVENSON, Reston (Apr. 22, '15) Asst. Prof. of Chemistry, The College of the City of N. Y., New York City.
STEWART, Harry M. (Sept. 27, '16) Supt. of Blast Furnaces, Carnegie Steel Co., Duquesne, Pa.
STEWART, Marshall E. (Oct. 21, '16) Works Mgr., Plant 3, Roessler & Hasslacher Chemical Co.; mailing address, 149 Kearney Ave., Perth Amboy, N. J.
STEWART, Reid T. (July 29, '10) Professor of Mechanical Engineering, University of Pittsburgh, Pittsburgh, Pa.; res., 1524 Shady Ave.
STEWART, Robert Stuart (Sept. 26, '08) Consult. Elec. Eng., 530 St. Paul Ave., Detroit, Mich.
STICHT, Robert C. (May 29, '09) General Mgr., Mt. Lyell M. & R. Co., Ltd., Queenstown, Tasmania, Australia.
ST. JOHN, H. M. (Mar. 24, '16) Res. Eng., Commonwealth Edison Co.; mailing address, 28 N. Market St., Chicago, Ill.
STOCKTON-ABBOTT, Lyle (July 28, '16) c/o Gulf Refining Co., Port Arthur, Texas.
STOLL, Clarence G. (Mar. 27, '09) Western Elec. Co., Hawthorne Station, Chicago, Ill.
STONE, Chas. A. (Apr. 3, '02) Stone & Webster, 147 Milk St., Boston, Mass.
STONE, George W. (Mar. 27, '09) c/o Hooker Electrochemical Co., Niagara Falls, N. Y.
STONE, I. F. (Jan. 29, '09) Pres., Nat. Aniline & Chemical Co., 100 William St., New York City.
STONE, Joseph P. (Nov. 21, '08) New Jersey Zinc Co., Franklin, N. J.; mailing address, P. O. Box 441, Franklin, N. J.
STONE, John Stone (Jan. 29, '09) Consult. Elec. Eng., 34 Gramercy Park, New York City.
STOREY, Oliver Wendell (Feb. 25, '11) Met. Eng., c/o C. F. Burgess Labs., Madison, Wis.
STOUGHTON, Bradley (Dec. 31, '09) Sec'y American Institute of Mining Engineers, 29 W. 39th St., New York City.
STRAUSS, Frank A. (Mar. 26, '15) Asst. in Electrochemistry, Columbia Univ., New York City; mailing address, 28 W. 70th St., New York City.
STUPAKOFF, S. H. (Feb. 27, '14) Manufacturer, 401-431 Amberson Ave, Pittsburgh, Pa.
STYRI, Haakon (Feb. 25, '11) Docent of the Metallurgy of Iron, Norges tekniske hoiskole, Trondhjem, Norway.
SUMMERS, Leland L. (Sept. 26, '08) L. L. Summers & Co., First Nat'l Bank Bldg., Chicago, Ill.
SWARTLEY, Henry P., Jr (June 1, '15) Sales Engineer, c/o Davis Bournonville Co., Marion Station, Jersey City, N. J.
SWENARTON, W. Hastings (Apr. 27, '12) Firm of Merwin & Swenarton, 2 Rector St., New York City.

SYMMES, Whitman (Dec. 4, 03) Consult. Chem. Eng., Virginia City, Nev.
TABER, Geo. H., Jr. (Dec. 30, '16) Chem. Eng., Gulf Refining Co.; mailing address, 4114 Grant Blvd., Pittsburgh, Pa.
TACHIHARA, Jin (Mar. 27, '14) Electrical Engineer, Mitsu Bishi Dockyard and Engine Wks., Kobe, Japan.
TADA, Kozo (July 28, '16) Supt. Power House, Inawashire Hydro-Elect. Power Co., c/o Bandai Post Office, Fukushimaken, Japan.
TADA, Commander S. (Sept. 4, '03) Naval Inspector's Office, Kawasaki Dockyard, Kobe, Japan.
TAFEL, Theodore, Jr. (Oct. 21, '16) Mgr., "Lucky Knock Mine," Tonasket, Wash.
TAGGART, Walter T. (Nov. 6, '02) University of Pennsylvania, Dept. of Chem., Philadelphia, Pa.
TAKAMINE, Jokichi (Feb. 27, '09) Research Chemist, Parke, Davis & Co., 550 W. 173d St., New York City.
TAKIKAWA, Yasuo (Oct. 21, '16) Member Asso. Chem. Industry, Tokyo, Japan; mailing address, 614 Chestnut St., So. Bethlehem, Pa.
TALBOT, Prof. H. P. (Jan. 8, '04) Prof. of Inorganic Chem., Mass. Inst. of Tech.; res., 273 Otis St., West Newton, Mass.
TANNER, W. Lee (Sept. 27, '16) Chief Chemist, New Castle Plant, Bethlehem Steel Co.; mailing address, Box 249, Wilmington, Del.
TATSUMI, Eiichi (Mar. 24, '16) Chem. Eng., Mitsui Mining Co., 25 Madison Ave., New York City.
TAYLOR, Dr. Chas. E. (May 29, '09) Taylor Chem. Co., Penn Yan, N. Y.
TAYLOR, Floyd D. (Dec. 31, '09) Canton, Pa.
TAYLOR, H. N. (Nov. 24, '16) Senior Member Firm, N. & G. Taylor Co.; mailing address, 300 Chestnut St., Philadelphia, Pa.
TAYLOR, Hugh S. (June 1, '15) Instructor in Physical Chem., Graduate College, Princeton, N. J.
TAYLOR, John B. (June 21, '11) Consulting Elec. Engr., 100 Broadway, New York City; mailing address, 23 Lowell Road, Schenectady, N. Y.
TEEPLE, Dr. J. E. (May 1, '06) Consulting and Mfg. Chemist, 50 East 41st St., New York City.
TEEPLE, Oliver J., Jr. (Feb. 26, '15) Tech. Asst., Du Pont Powder Co., 942 Du Pont Bldg., Wilmington, Del.
TEMPLE, Sterling (Sept. 27, '16) In charge of Industrial Chemistry Courses, Univ. of Minnesota; mailing address, 1758 Blair St., St. Paul, Minn.
THARALDSEN, Filip (Apr. 29, '11) General Mgr., A/S Ilens Smelteverk, Trondheim, Norway.
THATCHER, C. J., Ph.D. (Jan. 7, '05) Pat. Exp., No. 1 Riverdale Ave., New York City.
THOMAS, Bruno (June 28, '12) Consulting Engineer, 5026 University Blvd., Seattle,
THOMAS, Geo. E. (June 30, '16) Chemist and Electroplater, Factory H, International Silver Co.; mailing address, 759 Broad St., Meriden, Conn.
THOMPSON, Prof. Elihu (Sept. 17, '03) Elec., Gen. Elec. Co., 22 Monument Ave., Swampscott, Mass.
THOMPSON, J. G. (Feb. 25, '16) Asst. in Chemistry, Rockefeller Hall, Cornell Univ., Ithaca, N. Y.
THOMPSON, John (Feb. 27, '09) Civil and Mechanical Engineer, 253 Broadway, New York City.
THOMPSON, M. deK., Jr. (Nov. 6, '03) Associate Prof. of Electrochem., Mass. Inst. of Tech., Cambridge, Mass.
THOMPSON, Mack F. (Apr. 26, '16) Mgr., Prairie Grove Elec. Co., Prairie Grove, Arkansas.
THORDARSEN, Chester H. (Apr. 6, '11) President, Thordarsen Elec. Mfg. Co., 216-220 S. Jefferson St., Chicago, Ill.; res., 1416 Leland Ave.
THORNE, C. A. (May 22, '14) Consult. Engr., Ovre Slotsgate 5, Kristiania, Norway.
THRELFALL, Richard (Apr. 4, '03) Oakhurst, Church Road, Goghaston, Birmingham, England.
THUM, Wm. (Dec. 31, '14) Supt. of Electrolytic Smelt. Co., 44 Webb Street, Hammond, Ind.
THUNBER, John H. (Oct. 21, '16) Chemist and Assayer, Gorham Mfg. Co.; mailing address, 210 Lexington Ave., Providence, R. I.
THWING, Dr. Charles Burton (Nov. 27, '09) Pres., Thwing Instrument Co., 3339-41 Lancaster Ave., Philadelphia, Pa.
TIEMANN, Hugh P. (Oct. 24, '13) Asst. Metallurgical Eng., Carnegie Steel Co., 520 Carnegie Bldg., Pittsburgh, Pa.
TILLBERG, Erik W. (Nov 6, '02) Westervik, Sweden.
TILLMAN, Richard H. (Aug. 25, '16) Mgr., New Business Dept., Consolidated Gas, Electric Light and Power Co., Lexington and Liberty Sts., Baltimore, Md.
TINGBERG, Otto (July 29, '10) Editor of Jern-Kontorets Annaler, Jernkontoret, Stockholm, Sweden.
TOCH, Maximilian (Nov. 6, '03) 320 Fifth Ave., New York City.
TONE, F. J. (Apr. 3, '02) Works Mgr., The Carborundum Co., Niagara Falls, N. Y.
TORELL, T. F. (Aug. 28, '14) Chief Chemist & Asst. Supt., Kristiansand Nikkel raff. verk, Kristiansand, S. Norway.
TOWER, O. F. (Dec. 31, '14) Prof. of Chemistry, Adelbert College, Cleveland, Ohio.

TOWNEND, Robert V. (Dec. 31, '15) Res. Asst., c/o Standard Aniline Products Inc., Wappingers Falls, N. Y.
TOWNSEND, C. P. (Apr. 3, '02) 918 F St., N. W., Washington, D. C.
TRANTIN, Jacob, Jr. (Feb. 25, '16) Res. Met., Western Electric Co., 6223 Blackstone Ave., Chicago, Ill.
TUCKER, Samuel A. (Mar. 3, '06) Adjunct Prof. Electrochem., Columbia Univ.; res., 155 E. 61st St., New York City.
TURNBULL, Robert (Feb. 27, '09) Box 416, Welland, Ont., Canada.
TURNER, F. M., Jr. (Feb. 21, '13) Trinity College, Queen St., W., Toronto, Ont., Canada.
TURNER, M. R. (Oct. 27, '11) Manager & Chem., A/s Stangfjordens Elektromiske Fabriker, Gjorde, Stangfjorden pr. Bergen, Norway.
TURNOCK, L. C. (Nov. 26, '10) Dept. of Chemical Engineering, Carnegie Institute of Technology, Pittsburgh, Pa.
TURRENTINE, John W. (Oct. 29, 08) Bureau of Soils, Dept. of Agriculture, Washington, D. C.
TYLER, Walter S. (July 28, '16) Supt. Matrix Dept., American Graphophone Co., 503 Colorado Ave., Bridgeport, Conn.
UHLENHAUT, F., Jr. (May 26, '10) Chief Engineer, Allegheny County Light Co. and Pittsburgh Railways Co., 435 Sixth Ave., Pittsburgh, Pa.
UNDERWOOD, C. W. (Aug. 25, '16) District Mgr., Westinghouse Elec. & Mfg. Co., 780 Ellicott Square, Buffalo, N. Y.
UNGER, Geo. N. (Sept. 27, '16) Student, Purdue Univ., Box 104, West Lafayette, Ind.
UNGER, John S. (May 26, '10) Manager, Central Research Bureau, 1053-1057 Frick Annex Bldg., Pittsburgh, Pa.
UNGER, Magnus (Nov. 27, '09) Elec. Eng., The General Electric Co., Pittsfield, Mass.; res., 51 Lincoln Terrace.
VALENTINE, Irving R. (July 21, '11) Chemist, Research Laboratory, General Elec. Co., Schenectady, N. Y.; res., 15 Snowden Ave.
VALENTINE, Wm. (Sept. 17, '03) 22 Mitchell Ave., Waterbury, Conn.
VAN ARSDALE, Geo. D. (June 21, '11) Consulting Chemist, Phelps, Dodge & Co., 99 John St., New York City.
VAN BRUNT, Chas. (Feb. 27, '09) Chemist, Research Laboratory, General Electric Co., Schenectady, N. Y.
VAN DEVENTER, Harry R. (Feb. 27, '09) Elec. Engr., Sumter Tel. Mfg. Co., Sumter, S. C.
VAN KEUREN, Wm. L. (Dec. 31, '15) Eng., Edison Lamp Works, General Electric Co.; mailing address, 78 Danielson St., North Bergen, N. J.
VAN SICKLEN, Wm. J. (Oct. 22, '15) Instructor in Chemistry, Rice Institute, Houston, Texas.
VASSAR, H. S. (Oct. 22, '15) Lab. Eng., Public Service Elec. Co., 39 Willard Ave., Bloomfield, N. J.
VAUGHN, C. F. (Nov. 6, '02) Supt. Castner Electrolytic Alkali Co., University Club, Niagara Falls, N. Y.
VIOL, Chas. H. (Dec. 31, '15) Director, Radium Res. Lab., Standard Chem. Co.; mailing address, Box 22, Oakland Station, Pittsburgh, Pa.
VOM BAUR, Carl H. (Oct. 26, '12) 2043 Whitehall Bldg., New York City.
VON FOREGGER, R., Ph.D. (Sept. 2, '05) 31 W. 42d St., Aeolian Bldg., New York City.
VOORHEES, Louis A. (Apr. 3, '02) 111 Carroll Place, New Brunswick, N. J.
VORCE, L. D. (July 31, '07) Vice-Pres., Tennessee Copper Co., 2 Rector St., New York City.
WADDELL, Montgomery (Mar. 27, '09) Consulting Engr., 30 Church St., New York City.
WADSWORTH, Frank L. O. (July 1, '04) 1347 Oliver Bldg., Pittsburgh, Pa.
WAGNER, Henry L., M.D., Ph.D. (Apr. 3, '02) 518 Sutter St., San Francisco, Cal.
WALDO, Leonard (Nov. 4, '05) Consult. Eng., 49 Wall St., New York City.
WALDO, Wm. B. (June 21, '11) Consulting Eng., 7 East 42d St., New York City.
WALKER, Arthur L. (Feb. 27, '09) Prof. of Metallurgy, Columbia University, New York City.
WALKER, E. C., 3d (Oct. 22, '15) 191 Babcock St., Brookline, Mass.
WALKER, Geo. H. P. (Aug. 25, '16) Chief Chemist, Canadian Salt Co. Ltd.; mailing address, Box 248, Sandwich, Ontario, Canada.
WALKER, James W. (July 26, '12) Managing Director, Alexander Walker & Co., Marine Lodge, Irvine, Scotland.
WALKER, Dr. W. H. (Aug. 7, '02) Prof. Chem. Eng., Mass. Inst. of Tech., Cambridge, Mass.
WALLACE, Walter (Jan. 29, '09) Assistant Works Mgr., Oldbury El. Chem. Co., Niagara Falls, N. Y.
WALLOWER, Frank C. (Nov. 24, '16) 112 Sergeant Ave., Joplin, Mo.
WALMSLEY, Walter N. (Sept. 24, '10) Alabama Power Co., Brown-Marx Bldg., Birmingham, Ala.
WALSH, Philip C., Jr. (Apr. 7, '06) Member Walsh's Sons & Co., Metal and Machinery Merchants, 19 Grant St., Newark, N. J.
WALTER, R. J. (Sept. 27, '16) Consulting Mining and Met. Eng., Kittmas Mines Co.; mailing address, 2130 Downing St., Denver, Colo.

WALTERS, Joseph (Nov. 27, '14) Foreman Electroplater, The Southern Stove Works; mailing address, 2019 Park Ave., Richmond, Va.
WARD, A. T. (Apr. 26, '13) Experimental Eng., Braden Copper Co., Rancagua, Chile, So. America.
WARD, H. Lee (Dec. 30, '16) Instructor in Chemistry, School of Chem., Univ. of Minnesota, Minneapolis, Minn.
WARD, Louis E. (Mar. 25, '08) Rumford, Me.
WARING, Tracy D. (Apr. 6, '07) Standard Underground Cable Co., Perth Amboy, N. J.
WASHBURN, Frank S. (Oct. 29, '08) Pres., c/o American Cyanamid Co., 200 Fifth Ave., New York City.
WATERMAN, Frank N. (Apr. 3, '02) 100 Broadway, New York City.
WATKINS, W. H. (Dec. 31, '15) 116 Halleck Ave., Brooklyn, N. Y.
WATTS, Oliver P., Ph. D. (Mar. 5, '04) Asst. Prof. of Applied Electrochem., Univ. of Wisconsin; res,, 114 Spooner St., Madison, Wis.
WEAVER, W. D. (Apr. 3, '02) Charlottesville, Va.
WEBB, L. W. (Sept. 26, '08) Master Elect., Const. and Rep. Dept., Navy Yard, Norfolk, Va.
WEBER, Dr. M. G. (Apr. 29, '11) 76 Rutland Road, Brooklyn, N. Y.
WEBERT, Louis P. (Feb. 23, '12) Box 717, Bath, Me.
WEBSTER, Clement L. (Apr. 24, '09) Geologist and Mining Engr., The Interstate Investment and Development Co., Charles City, Floyd Co., Iowa; mailing address, 111 Hawkins Ave.
WEBSTER, Edwin S. (Apr. 3, '02) Stone & Webster, 147 Milk St., Boston, Mass.
WEEKS, Charles A. (Nov. 27, '09) The Forrest Bldg., 119 S. 4th St., Philadelphia, Pa.; res., 2006 N. 20th St.
WEEKS, F. D. (May 27, '11) Smelter Supt., The Ohio and Colorado Smelt. and Ref. Co., Salida, Col.; mailing address, c/o Metallurgical Co. of America, 52 Broadway, New York City.
WEIMER, Edgar A. (Jan. 29, '09) Pres. and Supt., Weimer Machine Co., Lebanon, Pa.
WEINTRAUB, Ezechiel (Oct. 29, '08) 9 Everett St., Cambridge, Mass.
WEISENBURG, Andrew (Feb. 23, '12) Placer Examination in Colombia, South America; mailing address, 2030 Chestnut St., Philadelphia, Pa.
WEISER, Harry B. (Sept. 27, '16) Instructor in Chem., The Rice Institute, Houston, Texas.
WEISSENBURGER, G. E. (Dec. 31, '15) Pres., Keokuk Electro-Metals Co., Keokuk, Iowa.
WEITLANER, R. J. (Apr. 6, '11) Hess Steel Co., Baltimore, Md.
WEITZ, A. H. (July 25, '15) Pionesta Valley Chemical Co., Mayburg, Pa.
WELLMAN, S. T. (Apr. 6, '11) Chairm., Wellman, Seaver, Morgan Co., 1878 E. 90th St., Cleveland, Ohio.
WELLS, Prof. J. S. C. (Nov. 6, '14) Consult. Eng., 105 Thomas St., Cranford, N. J.
WEN, Ching Yu (June 21, '11) 15B. Jessfield Road, Shanghai, China.
WENDT, Gerald L. (Sept. 27, '16) Instructor, The Rice Institute, Chemical Lab., Houston, Texas.
WENNER, R. S. (Dec. 26, '13) Elec. Engr., 540 N. 6th St., Allentown, Pa.
WENTWORTH, H. A. (Jan. 23, '14) Tech. Director, American Zinc, Lead and Smelting Co., 55 Congress St., Boston, Mass.
WERBY, A. B. (Mar. 23, '12) c/o Werby Labs., 29 Central St., Boston, Mass.
WESSON, David (May 1, '06) Mgr. of Tech. Dept., The Southern Cotton Oil Co., 111 So. Mountain St., Montclair, N. J.
WESTON, Edw., Sc.D., LL.D. 645 High St., Newark, N. J.
WETTSTEIN, Thos. F. (Oct. 22, '15) Res. Dept., United Lead Co., New York City; mailing address, Box 415.
WHEELER, A. E. (Feb. 6, '04) c/o Robt. Williams & Co., Friars House, New Broad St., London, E. C., England.
WHEELER, Fred B. (Apr. 24, '09) Consult. Engineer, Stepney Depot, Conn.
WHITAKER, A. W., Jr. (Feb. 25, '16) Research Eng., Aluminum Co. of America, Works No. 1, Niagara Falls, N. Y.
WHITAKER, M. C. (May 22, '14) Prof. of Chem., Columbia Univ., New York City.
WHITE, Albert R. (Jan. 28, '11) Mich. Electrochemical Co., Menominee, Mich.
WHITE, Edmond A. (July 31, '08) Const. Eng., The Electrolytic Ref. and Smelt. Co., Port Kembla, N. S. W., Australia.
WHITE, Frederick L. (May 5, '10) Research Associate, 1543 Wyandotte Ave., Lakewood, Ohio.
WHITE, Harold E. (Aug. 25, '16) Asst. in Res. Dept., The Norton Co.; mailing address, 516 Elmwood Ave., Buffalo, N. Y.
WHITE, J. G. (Sept. 4, '03) Pres., J. G. White & Co., 43-49 Exchange Place, New York; chairman of J. G. White Co., Ltd., 22A College Hill, London, E. C., England; res., 440 West End Ave., New York City.
WHITE, R. H. (Oct. 2, '02) Research Eng., c/o Norton Co., Niagara Falls, N. Y.
WHITLOCK, E. H. (May 9, '03) Gen. Supt., The Sandusky Portland Cement Co., 818 Engineers Bldg., Cleveland, Ohio; mailing address, 11200 Edgewater Drive.
WHITNEY, Dr. W. R. (Apr. 3, '02) General Elec. Co., Schenectady, New York.
WHITTEN, Wm. M. (Apr. 3, '02) 727 du Pont Bldg., Wilmington, Del.

WICKES, Clarence S. (May 26, '10) Superintendent, Record Factory, Victor Talking Machine Co., Philadelphia; res., 28 Franklin Ave., Merchantville, N. J.
WIECHMANN, F. G. (Apr. 3, '02) Consulting and Research Chemist, 90 West St., New York City.
WIGGLESWORTH, Henry (June 6, '03) Mfg. Chem., General Chem. Co., 25 Broad St., New York City.
WILCOX, W. G. (Sept. 28, '12) c/o Aluminum Co. of America, Massena, N. Y.
WILDER, Frederic L. (Feb. 6, '04) Morro Velho, Villa Nova de Lima, Minas Geraes, Brazil.
WILEY, Brent (May 29, '09) Commercial Engr., Westinghouse Elec. & Mfg. Co.; mailing address, 905 Maryland Ave., Pittsburgh, Pa.
WILKE, William (Feb. 27, '09) Chemical Engineer, 86 Norwood Ave., Buffalo, N. Y.
WILKINSON, W. N. (Oct. 22, '15) Asst, Secy., Mgr. of Sales, Union Sulphur Co., 17 Battery Place, New York City.
WILLARD, Frederic W. (Nov. 26, '10) Eng. of Chem. Methods, Western Elec. Co., Inc., Chicago, Ill.; mailing address, 506 N. Elmwood Ave., Oak Park, Ill.
WILLARD, Dr. H. H. (Feb. 6, '04) Asst. Prof., Analytical Chemistry, University of Michigan, Ann Arbor, Mich.; res., 802 Monroe St.
WILLEY, Leland M. (June 29, '07) Chemist, Gen. Elec. Co., Schenectady, N. Y.; res., 230 Liberty St.
WILLIAMS, Arthur (Sept. 26, '08) c/o New York Edison Co., 55 Duane St., New York City.
WILLIAMS, Clyde E. (Nov. 24, '16) Special Chemist, Union Assay Office, 1057 Lake St., Salt Lake City, Utah.
WILLIAMS, Egbert R. (Nov. 30, '12) Yorktown, Va.
WILLIAMS, Harry J. (Mar. 3, '06) 12 Rosemont St., Worcester, Mass.
WILLIAMS, John T. (Apr. 2, '04) 100 Broadway, New York City.
WILLIAMS, Frank M. (June 28, '12) Consulting Chemical Engr., 177 Mullin St., Watertown, N. Y.; res., 43-44 Sherman Bldg., Watertown, N. Y.
WILLIAMS, Naboth O. (Nov 26, '15) 20 East Park St., Newark, N. J.
WILLIAMSON, A. M. (Nov. 26, '07) Gen. Supt., Inter. Acheson Graphite Co., Niagara Falls, N. Y.
WILLS, Wm. H., Jr. (Apr. 22, '15) 437 South Ave., Wilkinsburg, Pa.
WILSON, C. H. (Oct. 22, '15) Pres., Wilson-Maeulen Co., 65 Second Ave., Mt. Vernon, N. Y.
WILSON, Irving W. (Jan. 28, '11) Asst. Supt., Aluminum Co. of America, Massena, N. Y.
WILSON, J. Rattray (Jan. 29, '09) El. Eng., 135 Wellington Road, Buffalo, N. Y.
WILSON, N. A. (Oct. 22, '15) Asst. Supt., Norton Co. of N. Y.; mailing address, P. O. Box 202, La Salle, N. Y.
WINDER, C. A. (May 22, '14) Res. Agt., General Electric Co.; mailing address, 52 Gluck Bldg., Niagara Falls, N. Y.
WINNINGHOFF, W. J. (Dec. 31, '15) Chemist, 71 Lenox Ave., E. Orange, N. J.
WINSHIP, Dr. Walter E. (Aug. 5, '05) Gen. Mgr., 612 W. 112th St., New York City.
WINSLOW, C. V. (Apr. 2, '13) Foreman Electroplater, Turner and Seymour Co., 536 South Main St., Torrington, Conn.
WINSLOW, Fred. E. (Feb. 27, '09) 151 N. Central Ave., Chicago, Ill.
WINTER, E. J. (Apr. 22, '15) Designing Eng., American Cyanamid Co.; mailing address, 84 Beech St., Flushing, Long Island, N. Y.
WIRT, Chas. (July 26, '12) Pres., Wirt Co., Philadelphia, Pa.; mailing address, 508 E. Washington Ave., Germantown, Pa.
WITHERELL, Chas. S. (July 25, '13) Met. Eng., c/o The Chile Exploration Co., 120 Broadway, New York City.
WITHERSPOON, R. A. (Oct. 2, '02) Shawinigan Carbide Co., Shawinigan Falls, Quebec, Canada.
WITHERSPOON, T. A. (Apr. 3, '02) Nat. Union Bldg., 918 F. St., Washington, D. C.
WITHROW, James R. (May 29, '09) Prof. Industrial Chemistry, Ohio State University, Columbus, Ohio.
WOHLWILL, Dr. Heinrich (June 29, '07) Norddeutsche Raffinerie, Elbstr. 35, Hamburg, Germany.
WOLF, Edgar J. (Aug. 26, '10) Mt. Vernon, Ind.
WOLF, Harry J. (Sept. 7, '06) Min. Eng., First National Bank Bldg., Denver, Colo.; mailing address, 1510 Washington, Ave., Golden, Colo.
WOOD, E. F. (Apr. 3, '02) Vice-Pres., Int. Nickel Co., 43 Exchange Pl., New York City.
WOOD, Prof. H. P. (Jan. 5, '07) Prof. Elec. Eng., Georgia Technical School, Atlanta, Ga.
WOODSIDE, F. C. (Apr. 26, '13) Chief Chemist, General Elec. Co., Pittsfield, Mass.; res., 831 North St.
WOODWARD, J. M. (May 6, '05) Nela Park, Cleveland, Ohio.
WOODWORTH, S. E. (Oct. 22, '15) Metallurgist, with Chas. Butters, 419 Embarcadeso, San Francisco, Cal.
WOOLDRIDGE, Wm. J. (Nov. 21, '08) Gen. Elec. Co., 134 Appleton Ave., Pittsfield, Mass.

WORTH, B. G. (May 26, '10) Electrical Engineer, Walter Kidde, Engineer-Contractor, 120 Cedar St., New York City; residence, 1212 Martine Ave., Plainfield, N. J.

WRIGHT, Arthur (Apr. 27, '12) Lawyer, Firm of Prindle, Wright & Small, 111 Broadway, New York City; res., 45 Markwood Road, Forest Hills Garden, L. I., N. Y.

WRIGHT, J. C. (Sept. 15, '15) 48 West 94th St., New York City.

WRINKLE, Noah (Sept. 27, '16) Supt. of Plant, National Soda Products Co.; mailing address, Keeler, Inyo Co., Cal.

WURSTER, Oscar H. (May 27, '11) c/o Morris & Co., Union Stock Yards, Chicago, Ill.

WYMAN, Walter S. (Mar. 27, '14) Treasurer & Gen. Mgr., Central Maine Power Co., 49 Western Ave., Augusta, Maine.

YAGER, John J. (Dec. 31, '15) Sales Eng., Buffalo Forge Co.; mailing address, 268 Carlton St., Buffalo, N. Y.

YAMASAKI, Dr. Jingoro (Apr. 29, '11) Yonezawa Higher Technical School, Yonezawa, Japan; res., Tokio, Japan.

YATSEVITCH, Michael (Feb. 23, '12) Metallurgical Lab., Polytechnical Inst., Kiev, Russia.

YNGSTROM, Lars (Dec. 31, '10) Owner of Sandsta Elektriska Smältwerk, Haggo, Sweden.

YOSHIKAWA, Prof. Kamejiro (Dec. 27, '07) Nakasuji Ishuyakushi, Kyoto, Japan.

YOUNG, Hayes W. (July 25, '13) Instructor Stanford Univ., Stanford University P. O., Cal.

YOUNT, Andrew S. (June 1, 1915) Chemist, Experimental Station, Du Pont Powder Co., Wilmington, Del.; mailing address, 1022 Jackson St.

YUNCK, John A. (Apr. 30, '08) Electrometallurgist, 375 Ogden St., Newark, N. J.; mailing address, 422 Meeker St., South Orange, N. J.

ZAREMBA, Edward (Jan. 28, '08) 707 D. S. Morgan Bldg., Buffalo, N. Y.

ZELLER, Richard (Apr. 24, '14) Factory Mgr., Egyptian Lacquer Mfg. Co., Rahway, New Jersey; mailing address, 595 West End Ave., New York City.

ZIEGEL, Henry (Feb. 27, '14) 86 Longwood Ave., Brookline, Mass.

ZIMMERMAN, J. G. (Nov. 6, '02) Engineer in Experimental and Res. Dept., Sumter Electrical Works, Sumter, South Carolina.

ZIMMERMANN, Dr. Fritz (June 29, '07) c|o Baker & Co., Inc., Platinum Works, Murray St., Newark, New Jersey.

ZWINGENBERGER, Otto K. (Jan. 27, '12) Chemist, Patent Dept., Roessler & Hasslacher Chem. Co., Perth Amboy, N. J.

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Lawrence, J. N.
Mattern, G. G.
Patch, N. K. B.
Rippel, E. G.
Schwarz, T. L.
Schoellkopf, J. F., Jr.
Skillman, V.
Stephenson, H. L.

NEW YORK—Continued

Buffalo—Continued
Underwood, C. W.
Watkins, W. H.
White, H. E.
Wilke, Wm.
Wilson, J. R.
Yager, J. J.
Zaremba, Edward

Clinton—
Saunders, A. P.

Flushing (L. I.)—
Winter, E. J.

Glens Falls—
Hilliard, John D.

Gouverneur—
Brindley, G. F.

Ithaca—
Bancroft, W. D.
Bennett, C. W.
Gillett, H. W.
Lohr, J. M.
McBerty, F. H.
Thompson, J. G.

Katonah—
Le Boutillier, C.

Kenwood—
Reeve, A. G.

LaSalle—
Sneath, Wm. H.
Wilson, N. A.

Lockport—
Howard, L. E.
Kenan, W. R., Jr.

Massena—
Doerschuk, V. C.
Hall, H. M.
Little, W. T.
Scott, L. C.
Somdal, J. A.
Wilcox, W. G.
Wilson, I. W.

Menands—
Shiverick, M. D.

Monticello—
Isakovics, A. von

Mt. Vernon—
Brown, C. J.
Dabolt, N. E.
Wilson, C. H.

New Brighton—
Burger, Alfred

New Rochelle—
Castle, S. N.

New York City—
Abbé, P. O.
Acheson, E. G.
Addicks, L.
Allen, O. F.
Allyn, R. S.
Aldridge, W. H.
Atwater, C. G.
Baker, H. A.
Barnes, H. H., Jr.
Barrows, F. E.
Barstow, W. S.
Baskerville, C.
Beck, E. A.
Bedell, E. H.
Bergen, R. C.
Boeck, P. A.
Bogue, C. J.
Bowman, W.
Bradley, Linn

NEW YORK—Continued

New York City—Continued
Bradley, W. E. F.
Breneman, A. A.
Brown, H. P.
Browne, D. H.
Browne, deCourcy B.
Buck, H. W.
Cameron, W. S.
Canet, B. Chas.
Carse, D. B.
Case, W. E.
Chandler, C. F.
Child, Ernest
Clark, W. G.
Clark, W. J.
Cleaves, M. A.
Coho, H. B.
Cohoe, W. P.
Colcord, F. F.
Cooper, K. F.
Corning, C. R.
Crocker, J. R.
Deppe, W. P.
Dixon, Jos. L.
Doerflinger, W. F.
Doremus, C. A.
Dorr, J. V. N.
Douglas, James
Dreyfus, W.
Dwight, Arthur S.
Eimer, A.
Emerson, H.
Engelhard, C.
Eurich, E. F.
FitzGibbon, R.
Fliess, R. A.
Foley, C. B.
Frank, K. G.
Freas, Thos. B.
Frederick, G. E., Jr.
Fries, H. H.
Gaines, R. H.
Goepel, C. P.
Gray, J. H.
Grosvenor, W. M.
Guess, H. A.
Harris, J. W.
Hasslacher, J.
Hatzel, J. C.
Hendry, W. F.
Herty, C. H.
Hill, N. S., Jr.
Hirsch, Alcan
Hirschland, F. H.
Hoge, J. F. D.
Hunt, A. M.
Huntoon, L. D.
Ingalls, W. R.
Jacoby, H. E.
Jansen, E. W.
Johnson, J. E., Jr.
Joyce, C. M.
Kennedy, J. J.
Kern, E. F.
Kissock, Alan
Klipstein, E. C.
Knapp, Geo. O.
Kohn, M. M.
Kunz, G. F.
Landau, Alfred
Langton, J.
Leavitt, Wm. F. B.
Ledoux, A. R.
Liebmann, A. J.
Loebell, H. O.
Löve, E. G.

NEW YORK—Continued

New York City—Continued

Lovejoy, D. R.
Lucke, H. J.
MacDonald, J. A.
Magnus, Benjamin
Maier, C. G.
Mailloux, C. O.
Mantius, Otto
Martin, T. C.
Marvin, A. B.
Mason, F. S.
Mastick, S. C.
Mays, S. W.
McNeill, R.
Mershon, R. D.
Metz, H. A.
Moody, H. R.
Morey, S. R.
Morgan, J. L. R.
Morrow, J. T.
Morse, W. S.
Mortimer, J. D.
Muir, J. M.
Muschenheim, F. A.
Myers, W. S.
Nagelvoort, Adriaan
Nathan, A. F.
Nichols, W. H.
Nichols, W. S.
Ornstein, G.
Pennie, J. C.
Peters, F. F.
Petinot, N.
Price, E. F.
Prindle, E. J.
Prosser, H. A.
Reed, S. A.
Ricketts, L. D.
Riglander, M. M.
Riker, J. J.
Riley, L. A., 2d
Roeber, E. F.
Roller, F. W.
Rossi, A. J.
Roth, C. F.
Rowand, L. G.
Ruhl, L.
Schildhauer, Edw
Schloss, J. A.
Schuetz, F. F.
Schultz, L. C.
Scudder, H.
Seward, G. O.
Sharp, C. H.
Smith, E. A. C.
Speed, Buckner
Speiden, C. C.
Spilsbury, E. G.
Statham, Noel
Stevenson, Reston
Stone, I. F.
Stone, J. S.
Stoughton, Bradley
Strauss, F. A.
Swenarton, W. H.
Takamine, J.
Tatsumi, E.
Taylor, J. R.
Teeple, J. E.
Thatcher, C. J.
Thompson, J.
Toch, M.
Tucker, S. A.
Van Arsdale, G. D.
Vom Baur, C. H.
Von Foregger, Richard

NEW YORK—Continued

New York City—Continued

Vorce, L. D.
Waddell, M.
Waldo, Leonard
Waldo, W. B.
Walker, A. L.
Washburn, F. S.
Waterman, F. N.
Weeks, F. D.
Whitaker, M. C.
White, J. G.
Wiechmann, F. G.
Wigglesworth, H.
Wilkinson, W. N.
Williams, A.
Williams, J. T.
Winship, W. E.
Witherell, C. S.
Wood, E. F.
Wright, Arthur
Wright, J. C.
Zeller, R.

Niagara Falls—

Baker, E. M.
Barclay, E. H.
Barton, P. P.
Bayard, R. A.
Becket, F. M.
Blanchard, H. J.
Bliss, Wm. Lord
Callahan, J. F.
Carveth, H. R.
Cole, E. R.
Converse, V. G.
Cox, G. E.
Dunlap, O. E.
Edmands, I. R.
FitzGerald, F. A. J.
Fowler, R. E.
Frary, F. C.
Fuller, G. P.
Gegenheimer, R. E.
Geyler, F. O.
Gilbert, H. N.
Glaze, John B.
Glennie, R. D.
Griffith, J. R.
Hamann, A. M.
Harper, J. L.
Herzog, G. K.
Hinckley, A. T.
Horry, W. S.
Hooker, A. H.
Hutchins, Otis
Imlay, L. E.
Ishikawa, I.
Johnson, J. A.
Kellogg, H. W.
Koethen, F. L.
Lansing, C. N.
Lavene, H. A.
Lebherz, John
Leffel, C. E.
Lidbury, F. A.
Lyster, T. L. B.
MacMahon, J.
MacMahon, J. D.
MacMillan, J. R.
Marshall, J. G.
Mauran, M.
McKnight, W. A.
Meredith, W. F.
Moritz, C. H.
Moyer, G. C.
Mueser, Emil
Neuhaus, R.

NEW YORK—Continued

Niagara Falls—Continued
Noyes, H. L.
Nutting, E. G.
Osborne, S. E.
Phillips, R.
Rhodin, B. E. F.
Richardson, C. N.
Ritter, B. H.
Rowland, J. M.
Russell, C. A.
Saunders, L. E.
Schoellkopf, P. A.
Sergeant, E. M.
Simmers, A. L.
Smith, A.
Smith, E. S.
Snowdon, R. C.
Speiden, E. C.
Stamps, F. A.
Stone, G. W.
Tone, F. J.
Vaughn, C. F.
Wallace, W.
Whitaker, A. W., Jr.
White, R. H.
Williamson, A. M.
Winder, C. A.

Oneida—
Bailey, R. O.

Ossining—
Acker, Chas. E.

Piermont—
Main, W.

Penn Yan—
Taylor, C. E.

Prince Bay (L. I.)—
Johnston, F. A.
Johnston, W. A.

Richmond Hill (L. I.)—
Haslwanter, C.
Herreshoff, J. B.
Smull, J. G.

Rochester—
Hutchings, J. T.
Lee, I. E.
Schwarz, R. C.

Rome—
Parish, R. R.

Schenectady—
Andrews, W. S.
Arsem, W. C.
Berg, E. J.
Coffin, F. P.
Coolidge, Wm. D.
Creighton, E. E.
Hawkins, L. A.
Langmuir, I.
Murphy, E. J.
Reist, H. G.
Rushmore, D. B.
Seede, J. A.
Steinmetz, C. P.
Taylor, J. B.
Valentine, I. R.
Van Brunt, C.
Whitney, W. R.
Willey, L. M.

Syracuse—
Brookfield, W. B.
Conklin, E. B.
Cooper, H. C.
Harvey, F. A.
Matthews, J. A.
Pennock, J. D.

NEW YORK—Continued

Tonawanda—
DeForest, C. M.

Troy—
Bryson, T. A.
Hunter, M. A.
Lincoln, A. T.
Patton, D. C.

Wappingers Falls—
Townend, R. V.

Watertown—
Williams, F. M.

Williamsville—
Cushing, H. M.

Woodhaven—
Cox, H. N.

Yonkers—
Baekeland, L. H.
Duurloo, F.
Harrington, E. I.

NORTH CAROLINA

Asheville—
Betts, A. G.

Charlotte—
Gilchrist, P. S.

Clemmons—
Pickens, Rufus H.

West Raleigh—
Browne, W. H.

Whitney—
Kemmer, F. R.
Marseilles, Wm. P.

OHIO

Akron—
Shaw, E. C.

Alliance—
Baily, T. F.
Cope, F. T.
Foster, C. L.

Amherst—
Briggs, F. H.

Barberton—
Austin, A. O.

Canton—
Meyer, R.
Reese, P. P.

Cincinnati—
Davison, A. W.
Dittmar, Carl
Ecker, Howard, Jr.
Elliott, Geo. K.
Roessler, E. B.

Cleveland—
Brown, J. W.
Chapin, H. C.
Chillas, R. B., Jr.
Clymer, W. R.
Cook, Edw. B.
Crider, J. S.
Drefahl, L. C.
Fleming, S. H.
Graves, W. G.
Holmes, M. E.
Hyde, E. P.
Koehler, W.
Kranz, W. G.
Mainwaring, Wm. D.
Megroot, J. P.
Orr, C. A.
Pratt, E. B.

OHIO—Continued

Cleveland—Continued
Richardson, E. A.
Seguine, Wm., Jr.
Smith, A. W.
Tower, O. F.
Wellman, S. T.
Whitlock, E. H.
Woodward, J. M.

Columbus—
Daines, W. P.
Demorest, D. J.
Eldridge, S. E.
Flowers, A. E.
Leonard, G. M.
Withrow, J. R.

Dayton—
Clements, F. O.
Deeds, E. A.
Gerstle, John
Jack, G. B., Jr.
Niswonger, E. E.

Fostoria—
Downes, A. C.

Fremont—
Goodwin, J. H.

Lakewood—
Brooks, W. C.
Bullock, A. R.
Chaney, N. K.
Mann, W. W.
Moore, Wm. C.
Mott, W. R.
Ordway. D. L.
Pulman, O. S.
White, F. L.

Mansfield—
Darrah, W. A.

Massillon—
Kennedy, T. O.

Middletown—
Ahlbrandt, G. F.
Bate, H. A.

Napoleon—
Long, G. E.

Oberlin—
Crafts, W. N.

Portsmouth—
Kinnear, H. B.

Rittman—
Laib, Walter

Salem—
Davis, D. L.

Steubenville—
Barr, H. L.

Wadsworth—
Shapiro, H.

Youngstown—
Grossmann, M. A.

OREGON

Cornucopia—
Nestler, G. A.

Hood River—
Butcher, J. C.

Portland—
Hall, E. L.

PENNSYLVANIA

Allentown—
McCullough, H. F.
Wenner, R. S.

Altoona—
Casselberry, H.
Hanger, S. R.

Ambridge—
Farnham, F. F.
Meineke, O. H.

Aspinwall—
Hessom. B. F., Jr.

Bethlehem—
Fehnel, J. Wm.
Franklin, W. S.
Jacobson, B. H.

Boyerstown—
Corbin, J. R.

Brackenridge—
Connell, H. R.
Ober, J. E.

Braddock—
Lewis, J. D.

Bridgeville—
Saklatwalla, B. D.

Bryn Mawr—
Ely, T. N.

Canonsburg—
Guerber, A. J.
Morrison, W. L.

Canton—
Taylor, F. D.

Carnegie—
Ohlwiler, C. H.

Chester—
Comey, A. M.

Conshohocken—
Davis, F. W.

Coraopolis—
Hensen, Emil
Stafford, S. G.

Crafton—
Fawcett, L. H.

Creighton—
Cox, S. F.
Gelstharp, F.

Duquesne—
Stewart, H. M.

Easton—
Adamson, G. P.
Czarnechi, F. C.
Gordon, C. McC.
Hart, E.
Shimer, E. B.

East Pittsburgh—
Schoepf, T. H.
Skinner, C. E.

Ellwood City—
Dunn, J. J.
Offutt, J. W.

Emporium—
Snyder, J. L. K.

Gettysburg—
Parsons, L. A.

Harrisburg—
Calder, A. R.

Johnsonburg—
Buckie, H. H.

PENNSYLVANIA—Continued

Johnstown—
Appel, M.
Kenney, E. F.
Parkhurst, C. W.

Latrobe—
Garratt, Frank
Sessions, R. L.

Lebanon—
Weimer, E. A.

Marcus Hook—
Rittenhouse, Edw.

Mayburg—
Weitz, A. H.

McKeesport—
Clarke, E. B.
Goodspeed, G. M.

Munhall—
Hopkins, G. A.

New Castle—
Samuels, Wm. P.

Oakmont—
Fernekes, Gustave
Moore, J. R.

Palmerton—
Holstein, L. S.

Parnassus—
Blough, Earl

Philadelphia—
Arthur, Walter
Asef, Waldemar
Benoliel, S. D.
Bonine, Chas. E.
Breed, G.
Brophy, O.
Brown, R. P.
Buch, N. W.
Burman, B. F.
Callen, A. S.
Cary, C. R.
Clamer, G. H.
Corbin, J. R.
Devereux, W.
Eglin, W. C. L.
Fraley, J. C.
Furness, R.
Gerety, J. J
Gibbs, A. E.
Giles, I. K.
Goldbaum, J. S.
Hall, C. A.
Hering, C.
Hess, H.
Hicks, Edwin F.
Hitchcock, F. R. M.
Howard, G. M.
James, W. F.
Keith, N. S.
Kitsee, I.
Kutz, Milton
Lafore, J. A.
Lavino, E. J.
Lay, J. Tracy
Lukens, H. S.
McConnell, J. Y.
Merzbacher, Aaron
Meyer, J.
Moerk, F. N.
Morgan, Leonard P.
Ogden, John
Paul, H. N.
Rosengarten, G. D.
Russell, C. J.
Sadtler, S. P.

PENNSYLVANIA—Continued

Philadelphia—Continued
Sadtler, S. S.
Salom, P. G.
Schamberg, M.
Smith, E. F.
Smith, E. W.
Smith, H. F., Jr.
Stevens, J. F.
Taggart, W. T.
Taylor, H. N.
Thwing, C. B.
Weeks, C. A.
Weisenburg, Andrew
Wirt, Chas.

Pittsburgh—
Aston, James
Bacon, R. F.
Bear, S. L.
Bennett, B. F.
Brown, John T., Jr.
Connell, W. H.
Crabtree, F.
Dewey, B.
Dougherty, J. W.
Flannery, Jas. J.
Gibson, C. B.
Goodale, S. L.
Hartley, R. H.
Hibbert, Harold
Hitchcock, H. K.
Hurum, Fredrik
James, E. T.
James, J. H.
Kemery, P.
Kier, S. M.
Laughlin, H. H.
Lincoln, P. M.
Loeffler, Geo. O.
Mathias, D. L.
McDonald, R. A.
McKinley, Jos.
McNiff, G. P.
Meyers, H. H.
Moore, W. E.
Osborne, L. A.
Page, G. S.
Pinkerton, A.
Pope, Chas. E.
Ray, H. C.
Rodman, H.
Rypinski, M. C.
Sargent, G. W.
Schluederberg, C. G.
Slocum, F. L.
Speller, F. N.
Stahl, N.
Starr, A. B., Jr.
Stewart, R. T.
Stupakoff, S. H.
Taber, G. H., Jr.
Tiemann, H. P.
Turnock, L. C.
Uhlenhaut, F., Jr.
Unger, J. S.
Viol, C. H.
Wadsworth, F. L. O.
Wiley, B.

Primos—
Boericke, G.
Stein, W. M.

Reading—
Parker, Jas. H.

Roaring Springs—
McDonald, F.

PENNSYLVANIA—Continued

South Bethlehem—
Buck, C. A.
Butts, Allison
Hommel, R. P.
Kinter, G. R.
Kramer, L. B.
MacNutt, B.
Richards, J. W.
Roush, G. A.
Seyfert, S. S.
Takikawa, Y.

State College—
Dudley, Boyd, Jr.
Pond, G. G.

Steelton—
Reed, J. C.

Swarthmore—
Alleman, G.
Creighton, H. J.
Griffen, H. R.

Tarentum—
Parkinson, J. C.

Washington—
Morrison, M. E.

Wilkinsburg—
Adams, J. L., Jr.
Stephens, C. E.
Wills, Wm. H., Jr.

Wyncote—
Grübnau, G. M.

York—
Schleeder, L. B.

RHODE ISLAND

Greene—
Perry, C. M.

Newport—
Richards, E.

Providence—
Saunders, W. M.
Slade, W. C.
Thunber, J. H.

SOUTH CAROLINA

Columbia—
Mills, J. E.

Sumter—
Van Deventer, H. R.
Zimmermann, J. G.

SOUTH DAKOTA.

Deadwood—
Bowman, F. C.

Keystone—
Reinbold, Herman

TENNESSEE

Clarksville—
Foust, T. B.

Maryville—
Adams, T. J.
Glasscock, B. L.
Parks, R. E.

Memphis—
Holtzendorff, P. W.

TEXAS

Austin—
Harper, H. W.
Schoch, E. P.

El Paso—
Silverman, R. B.

Fort Worth—
Slater, W. A.

Houston—
Van Sicklen, Wm. J.
Weiser, H. B.
Wendt, G. L.

Port Arthur—
Alexander, C. M.
Detwiler, J. G.
Stockton-Abbott, L.

UTAH

Kanab—
Hayes, J. J.

La Sal—
Morgan, H. J.

Murray—
Hyde, R. W.

Provo City—
Smith, F. W.

Salt Lake City—
Austin, L. S.
Bradford, R. H.
Emery, W. L.
Hansen, C. A.
Letchfield, F. T.
Putnam, W. R.
Ralston, O. C.
Williams, C. E.

VERMONT

Northfield—
Howard, S. F.

VIRGINIA

Charlottesville—
Weaver, W. D.

Holcomb's Rock—
Lee, H. R.

Norfolk—
Webb, L. W.

Richmond—
Walters, Jos.

University—
Dunnington, F. P.

Yorktown—
Williams, E. R.

WASHINGTON

Pullman—
Skinner, H. J.

Seattle—
Crim, L. P.
Lyon, D. A.
Thomas, B.

Spokane—
Armstrong, L. K.
Keffer, Frederick

Tacoma—
Everette, W. E.

Tonasket—
Tafel, Theodore, Jr.

WEST VIRGINIA

Charleston—
Carrier, C. F., Jr.
Rollin, Hugh

Glen Ferris—
Huffard, J. B.

Morgantown—
Clark, F. E.
Hite, B. H.

Piedmont—
Randall, J. W. H.

St. Albans—
Sargent, R. N.

Warwood—
Bumgardner, J. W.

Weirton—
Rese, Wm. F.

WISCONSIN

Madison—
Burgess, C. F.
Hamister, V. C. H.
Helfrecht, A. J.
Kahlenberg, L.
Kowalke, O. L.
Low, F. S.
Pritz, W. B.
Ruhoff, O. E.
Schulte, W. B.
Storey, O. W.
Watts, O. P.

Milwaukee—
Bovee, B. A.
Gosrow, R. C.
Henderson, C. T.
Kremers, J. G.
Raeth, F. C.
Richardson, L. T.

WYOMING

Thermopolis—
Freeman, G. N.

CANADA.

BRITISH COLUMBIA

Nelson—
Fowler, S. S.

Trail—
Batchelder, J. K.
Hamilton, E. H.

Vancouver—
Barwick, W. S.
Hayward, R. F.
McIntosh, D.

MANITOBA

East Kildonan—
Baker, L. R.

Winnipeg—
Armes, H. P.
Morden, G. W.

NOVA SCOTIA

New Glasgow—
Cantley, T.
Dalton, A. C.

Sydney—
Collins, F. L.

ONTARIO

Belleville—
Green, S. S.

Kakabeka Falls—
Farrow, P. R.

Kingston—
Goodwin, L. F.
Goodwin, W. L.

Niagara Falls—
Arison, W. H.

Ojibway—
Baltzell, W. H.

Orangeville—
Deagle, L. M.

Sandwich—
Walker, G. H. P.

St. Catharines—
Heitmann, E.

Thorold—
Atwood, F. C.

Toronto—
Bain, J. W.
Barrows, W. S.
Boswell, W. O.
Burt-Gerrans, J. T.
Gaby, F. A.
Guess, G. A.
Kaemmerer, J. A.
Kenrick, F. B.
Mathewson, E. P.
Miller, W. L.
Moffat, J. W.
Turner, F. M., Jr.

Welland—
Carnegie, E.
Humbert, E. P.
Turnbull, R.

Windsor—
Henderson, E. G.

QUEBEC

Buckingham—
Hambley, F. J.

Montreal—
Davidson, T. R.
Hough, A.
Medbury, C. F.
Pascoe, C. F.
Spencer, A. G.
Stansfield, A.

Ottawa—
Haanel, E.
Lindsay, C. F.
Simpson, Louis

Quebec—
McKee, G. M.

Shawinigan Falls—
Acton, E. H.
Witherspoon, R. A.

CUBA.

Isle of Pines—
Roberts, I. L.

Jovellanos—
Weber, E. G.

SOUTH AMERICA.

BRAZIL

Rio de Janeiro—
De Medeiros. T. S. V.

S. Paulo—
De Souza. E.

Villa Nova de Lima—
Hill, Stafford
Jones, H.
Wilder, F. L.

CHILE

Chuquicamata—
Jörgensen, E. L.
Krog, Karl M.
McClenahan, J. S.
Merrill, M. W.

CHILE—Continued

Chuquicamata—Continued
Oldright, G. L.
Page, Wm. K.

Rancagua—
Harper, H. A.
Stevens, W. L.
Ward, A. T.

Santiago—
Antunez, V.
Diaz-Ossa, B.

PERU

Lima—
Boesch, J. E.
D'Ornellas, T. V.

AUSTRALASIA.

NEW SOUTH WALES

Broken Hill—
Gepp, H. W.

Port Kembla—
White, E. A.

Moonta Mines—
Hancock, H. L.

Sydney—
Murphy, R. K.

NEW ZEALAND

Christ Church—
Stark, E. E.

Dunedin—
Shepherd, F. R.

Epsom—
Gordon, H. A.

QUEENSLAND

Brisbane—
Henderson, J. B.
Jackson, A. G.

Mt. Morgan—
Johns, M. J.

SOUTH AUSTRALIA

Kooringa—
Du Faur, J. B.

VICTORIA

Melbourne—
Gillies, P. M.

TASMANIA

Queenstown—
Sticht, R. C.

ASIA.

CHINA

Lincheng—
Kwang, K. Y.

Shanghai—
Wen, C. Y.

JAPAN

Fuknoka—
Kaneko, K.

Fukushimaken—
Tada, Kozo

Kobe—
Murahashi, S.
Tachihara, Jin
Tada, S.

Kyoto—
Namba, M.
Nishikawa, Kikei
Yoshikawa, K.

Osaka—
Noguchi, Jun

Tajima—
Higashi, S.

Tokyo—
Igarashi, T.
Iwai, K.
Katsura, B.
Kameyama, Naoto
Kawamura, T.
Kishi, K.
Masujima, B.
Nohara, T.
Yamasaki, J.

AFRICA.

CAPE COLONY

Somerset, West—Quinan, K. B.

EUROPE.

AUSTRIA-HUNGARY

Brunn—
Babrowsky, G.

Budapest—
Pikler, A. H.

Treibach—
Fattinger, F.

Vienna—
Helfenstein, A.

BELGIUM

Brussels—
Cito, C. C.
Solvay, A.

Jemeppe—
Queneau, A. L. J.

Mons—
Henault, O-Dony.

Neerpelt—
Raeder, Bjorn

FRANCE

Paris—
deGeofroy, A.
Gall, H.
Keller, C. A.
Marie, C.
Ostheimer, J. W.

GERMANY

Berlin—
Finckh, Carl
Haber, Fritz

Bonn—
Bucherer, A. H.

Charlottenburg—
Engelhardt, V.
Reissenegger, H

Clausthal—
Hoffmann, R.

Dresden—
Schrey, A.

Essen-Ruhr—
Goldschmidt, Hans

Frankfurt—
De Neufville, R.

Hamburg—
Arnemann, P.
Wohlwill, H.

Hanau—
Heraeus, H.

Karlsruhe—
Askenasy, P.

Leipzig—
Schall, C.

Luebeck—
Draeger, A. B.

Nurnberg—
Forchheimer, P. J.

Schwerte—
Amberg, Richard

GREAT BRITAIN

Birmingham—
Threlfall, R.

Brimsdown—
Cornthwaite, H.

Cardiff, (Wales)—
Ewing, A. J.

Hatch End—
Jacob, A.

Irvine, (Scotland)—
Walker, J. W.

Liverpool—
Smith, A. T.

London—
Ashcroft, E. A.
Campbell, D. F.
Chalas, A.
Cowper-Coles, S.
Goldstein, P.
McBerty, F. R.
Merz, C. H.
Oakden, W. E.
Ruthenberg, M.
Sprague, E. C.
Wheeler, A. E.

Manchester—
Pring, J. N.

Sheffield—
Cutts, V. O.
Fawcett, P.
Hadfield, R. A.
Rowland, T.

Walthamstow—
Wilder, F. L.

ITALY

Aguila—
Dapples, A.

Ligure—
Giolitti, F.

Milan—
Rossi, C.

Rome—
Chiaraviglio, D.

NORWAY

Bergen—
Turner, M. R.

Christiania—
Bjornson, E.
Bryn, K.
Collett, E.
Collett, Ove
Goldschmidt, Heinrich
Hiorth, A.
Hiorth, F. V. L.
Hole, Ivar
Johansen, G. H.
Loken, Rikard
Olsen, T. S.
Söderberg, C. W.
Thorne, C. A.
Torell, T. F.

EUROPE—Continued.

NORWAY—Continued

Fredriksstad—
Moltkehansen, I. J.

Odda—
Giersten, S.

Rjukan—
Bonnevie, H.

Stavanger—
Bjorkstedt, Wm.
Jacobsen, F.

Trondhjem—
Farup, P.
Styri, H.
Tharaldsen, F.

Vadheim—
Kolkin, T. L.

RUSSIA

Abo (Finland)—
Aminoff, G.

Kiev—
Yatsevitch, M.

SPAIN

Huelva—
Shields, John

SWEDEN

Dannemora—
Leffler, J. A.

Falun—
Yngstrom, L.

SWEDEN—Continued

Gottenburg—
Olsson, Henning

Gullspang—
Hedlund, M.
Neumann, Wilhelm

Ludvika—
Groenwall, Assar

Mansbo—
Carlson, B.

Stockholm—
Forssell, J.
Ljungh, Hjalmar
Tingberg, Otto

Trollhattan—
Berglund, E. S.
Olaussen, K. O. E.

Uddeholm—
Lindberg, S. C.

Vesteras—
Edstrom, J. S.

Westervik—
Tillberg, E. W.

SWITZERLAND

Basel—
Fichter-Bernoulli, F.

Geneva—
Gandillon, A.
Guye, P. A.
Lacroix, H.

Turgi—
Landolt, H.

A symposium at the Thirtieth General Meeting of the American Electrochemical Society, held in New York City, September 28, 1916. Mr. F. A. Lidbury in the Chair.

"MADE IN AMERICA."

A symposium arranged and conducted by MR. L. E. SAUNDERS.

L. E. SAUNDERS: Several months ago a manufacturer of articles used in the electrochemical industry learned by accident that some of his products, which were being sold through dealers, were being put on the market as of European manufacture. A good deal of indignation was felt, and as a result all articles made by this company have since been marked with the maker's name and the fact that the articles were made in the United States.

This incident was the occasion for starting the movement which has resulted in this session. The Directors of the Society discussed the matter at some length, and it was decided that we should take account of stock at this time to see how our own particular industry is meeting the demands put upon it due to the shortage of products of European manufacture.

The field covered by the electrochemical industry is so broad that unless some dividing lines are drawn we might be obliged, at a discussion of this kind, to include almost anything manufactured in the country. We have been attempting to show in Niagara Falls the widespread and far-reaching character of the products manufactured there. This is also true of the products used in the electrochemical industry almost to as great an extent as in the case of the products manufactured. We have, therefore, in the preparation of this session endeavored to keep within comparatively narrow limits the subjects to be discussed so far as the more formal and preliminary preparation of papers is concerned. It is hoped that no limits whatever will be felt to be in existence in the personal discussion at this meeting.

The manner of going at the proposition has been to ask, first, the users of all sorts and kinds of articles to give their experience with those things made in the United States which have heretofore been purchased in whole or in part from abroad. Second,

an endeavor has been made to get the manufacturer to defend himself against possible adverse criticism by furnishing data which he, himself, has collected, probably in all cases showing the superiority of the articles he manufactures. In the course of this extensive correspondence many interesting sidelights have arisen, one of these being in connection with the mistaken notion that we were advocating a slogan, or adopting a trade-mark, instead of simply trying to find out where we stand. The words "Made in America" are being used to describe this session simply because they constitute a terse expression, and Mr. W. Acheson Smith will read you some thoughts on this phase of the subject which coincide with the opinions of the Committee, and, we think, with those of the Directors of the Society.

In order that we may have authoritative opinions on many of the articles made in America and made abroad, we have asked the Bureau of Standards to prepare a statement of those things which have come under its observation, and these are to be presented to us today by Mr. Schramm, of the Bureau, as a sort of starting point from which other *pro* and *con* statements can branch out.

I shall endeavor, in a perfectly neutral and unbiased manner, to quote from the extensive correspondence all the mud-slinging and honeyed words of praise which both the users and the manufacturers have indulged in. The object of making these statements is principally to introduce personal discussion, and unless in these various statements we succeed in making somebody very angry, this portion of the program will probably fail. It is also our intention to call on one or two unbiased persons who have opportunity and occasion to handle many different articles, from a dealer's standpoint, to make some statement as to their experiences with American made articles. But first, we must defend ourselves against such accusations as are contained in the following quotations from an extremely well-known member of this Society; afterwards we shall call on Mr. Smith to make our defense concerning the slogan idea.

I quote: "Personally, I should prefer to see the name of the individual or company on American products, and the letters U. S. A. in gold or flame or ink, or anything else good, rather than the words 'Made in America.' So far as I know, the people

who got up the scheme of 'Made in Germany' were real inventors of a fine slogan, and they also made the goods that made the slogan a fine slogan. There was no fake about it. Placing 'Made in America' on a lot of our stuff does not strike me favorably. Why imitate so perfectly as to use 'Made in America'? You know I am an idealist, but I have not carried it to such an extreme as to believe we are in Utopia, and that 'Made in America' at present would be sufficient guarantee of high quality."

Before calling on Mr. Smith I would call attention to the fact that the slogan "Made in Germany" does not necessarily carry any more perfect guarantee of quality than would a slogan "Made in America," and it is my personal observation that abuse has arisen in that case, and articles of inferior quality have been marketed under that slogan just as they might if the slogan "Made in America" were blindly used. The same objection of possible dishonesty may apply to both.

Another well-known member of this Society, on the other hand, believes that a "Made in America" movement should be carried on along the slogan idea. He believes that it is time for us to use American made material even though it is of somewhat inferior quality. He states: "Let us give the men in this country the making of things we require, and I am sure, when they have practiced as long as those in other countries, that the final product will be equal to if not better than that of foreign make." He further states: "I personally think we have all been educated to consider foreign made articles superior. We were taught in college that the words 'Made in Germany' carried a guarantee that this particular article was the best of its kind. I am now willing to start education in regard to American made articles."

Further reference to these subjects will be made as the discussion proceeds. I have now the pleasure of calling on Mr. Acheson Smith, of Niagara Falls.

Acheson Smith: The necessity for doing everything possible to "hold the trade," which the disturbed conditions in Europe have forced upon us, has resulted in many suggestions of more or less value. One suggestion which has apparently met with considerable favor is to use an expression such as "Made in America" or "Made in U. S. A." on manufactured articles, or their con-

tainers, and a bill[1] has been introduced into Congress providing for a national trade-mark which manufacturers may use by making the proper application and paying the necessary fee. The interest in this subject is of course aroused by the desire to extend our foreign trade and the use of American made products in the United States in preference to those imported.

The use of such an expression as "Made in America" may have a value in two ways. First, it might induce the use of American made goods through patriotic motives, and second, it might focus the attention of the purchaser upon the fact that the goods are made in America, and thereby perhaps cause him to prefer them to articles made elsewhere. If the appeal is made on patriotic grounds, it would certainly apply only to citizens of the United States, for citizens of other countries could not be expected to be influenced by such a plea. Even supposing, however, that a large number of Americans are thus influenced to use American goods in preference to foreign made we would have a condition, should foreign made goods be better, where an appeal to patriotism was used to stem the natural flow of trade, and thereby set up a rather flimsy artificial barrier which would soon be destroyed by the force of economy. It would therefore seem that this appeal would be limited to Americans and be of very doubtful value in inducing them to continue to use American goods.

If the expression "Made in America" is simply to focus the attention of people, both at home and abroad, upon the fact that the goods are made in America, it would seem axiomatic that such goods must be of the very highest possible quality and sold at a reasonable price, or the expression "Made in America," would soon be a warning against American made goods instead of an argument therefor. If the slogan "Made in America" could be limited to goods of the highest possible quality, which would have to have the approval of some central body or governmental bureau before the makers were permitted to use such expression, the slogan might become a sort of hall mark for quality, which would in time induce many people to demand American made goods upon the assumption that everything bearing the expression "Made in America" was of the highest quality. Unfortunately, it does not seem possible to establish standards by which every

[1] H. R. 16873, introduced by Mr. Kitchen.

article of manufacture can be measured, nor any bureau to which it would be safe to give the power of granting or withholding permission to use "Made in America." If the manufacturers of the best goods produced in America should use the expression "Made in America," we would naturally expect others who had difficulty in selling their goods, owing to poor quality or unreliability, to use the same slogan as a cloak to enable them to gain a standing which they do not deserve. If this should continue to any great extent, and it seems that it would be a very probable tendency, the use of the expression "Made in America" would likely be of more harm than benefit to American goods, for the simple reason that comparatively few instances of inferior quality would become more widely known and be remembered longer than many times the number of cases of high quality goods which have given satisfaction. It would simply be a case of bad news traveling faster than good news.

The whole question of selling goods in foreign countries is one of economics, and not a question of national trade-mark. As a nation, the value of our imports must equal our exports, so we will probably continue to import the goods we do not produce, or which are of a better quality than we make, and we will continue to export the goods others do not make, or which are preferred owing to their quality. As other countries may commence at some time to manufacture goods formerly imported, it would therefore seem evident that the only part of our foreign trade that is secure is the portion based on quality. If we manufacture and sell inferior articles, they cannot be a dependable part of our foreign trade.

One of the fundamental items in preparation for export trade is for a manufacturer to test his product in comparison with similar products made in other countries, and if his article does not prove to be the best, he should go back over his manufacture and leave nothing undone to make his output of a better quality than that of his competitors. Having thus made sure by *actual test* that his product is as good as or better than competing articles, he should take pride in placing *his own name and trade-mark* thereon so that his product may be identified, and if he is then willing to stand squarely behind his product he will have done the most important thing that can be done for himself and for

the foreign trade of the United States. If the manufacturers are desirous of gaining or extending their trade in other countries, they should be willing to put their goods to the *supreme test of actual comparison,* and when their goods are able to stand up under such test, they are then prepared to enter the foreign field, having their business based on the bed rock of quality. Any success which follows they will of course enjoy and the benefit to the United States will naturally ensue.

L. E. SAUNDERS: As has been mentioned before, the Bureau of Standards kindly consented to prepare a statement on investigations conducted by the Bureau upon articles made in this country, and Mr. Edward Schramm of the Bureau will now present this authoritative information, which we must all agree is of a neutral and unbiased nature.

EDWARD SCHRAMM: The following information is made public by permission of the Director of the Bureau of Standards. In considering the relation of the Bureau of Standards to things "Made in America," we must make clear at the outset that its primary contribution lies not so much in the development of special products as in the acquisition of knowledge through tests and investigations, and the spread of information by means of publications and a large correspondence. To cover the broad field of the Bureau's work lies quite without the scope of this review, and a few examples must suffice to indicate the nature of its activities. Within the past few years, the testing and certification of radium products has been undertaken; this work has enabled the purchaser to discover exactly what he was getting and has thus removed the element of uncertainty and danger of fraud from the industry. The preparation and sending out of standard samples of materials of certified composition or properties by means of which laboratories may easily check their methods of analysis or testing is an important part of the Bureau's work. The Bureau is co-operating with technical and scientific societies and manufacturers in the attack on certain important problems of industrial interest, among them the following: a comparative study of the effect on quality of rails of several methods of producing ingots; an investigation of the factors influencing the operation of electrotyping baths; investigations of methods

of minimizing the destructive action of stray electric currents on underground structures; investigations of the fire-resisting properties of structural materials, in co-operation with the Fire Underwriters and Mutual Laboratories and various engineering and industrial societies and associations; investigations relating to the elastic properties of steel columns in co-operation with the American Society of Civil Engineers and the American Railway Engineering Association.

Leaving these broader aspects of the work of the Bureau the remainder of this review will be devoted to a field in which it has a special and immediate interest, that of instruments and materials for scientific uses. In what follows, a necessarily brief account is given of some of the Bureau's experiences with such products.

Measures of mass, length, and volume: Let us consider first the fundamental measurements of mass and length. Balances and weights of the same grades as those obtained in Europe have been made in this country for many years. Many foreign balances have been imported in the past because of their lower prices, and some because of the reputation of the makers, but only a few special types could not be obtained in this country. The war has made no apparent changes except greatly increased production. With regard to volumetric glassware the situation appears to be that American makers can make fine apparatus if they will, but that they find greater profit in the bulk production of common articles, a statement which applies to many other lines. For tapes and other measures of length there is a tendency to replace ordinary steel by iron-nickel alloys. The dimensions of the alloy containing 36 percent nickel along with small amounts of manganese, silicon, and chromium, in all about 1 percent, were found by Guillaume to remain almost invariable with ordinary atmospheric changes of temperatures. For this reason it was called "Invar," and has been manufactured under that name in France. The Bureau of Standards is conducting an investigation in co-operation with a steel company for the purpose of producing American steels of specified thermal expansivity, combined with stability of dimensions and other desirable properties. At present steels of small expansivity are being studied to determine the effect of

various thermal, magnetic, and mechanical treatments as well as of slight variations in the constituents. This has already resulted in the production of specimens which, as far as small expansivity is concerned, compare favorably with good French Invar; but as yet sufficient time has not elapsed to show how stable they can be made in regard to constancy of length. An important material, the supply of which was cut off by the war, is the finer grade of sieve cloth used in the testing of cement and similar products. American manufacturers are making every effort to duplicate this cloth, but some of their product appears lacking in the desired uniformity. An alternative method of cement analysis depending on blowing out the fine particles by a current of air has been investigated in the cement laboratory of the Bureau. While requiring more elaborate apparatus and greater time than the sieve separation, it has the advantage of subdividing the material which would pass a 200-mesh sieve into four grades of fineness, thus giving a measure of the impalpable powder which constitutes the true active material of the cement. The method ought also to be useful in the testing of abrasives.

Electrical instruments: America has always taken a leading place in the production of commercial electrical measuring devices, only a very small quantity being imported. Watt-hour meters, both the alternating and the direct current type were originally developed in this country, and are now being produced in enormous quantities by elaborate factory methods. Together with ampere-hour meters they are now being exported, even to Europe, in large quantities.

As in many other industries, one of the most characteristic features of American manufacture is quantity production. In many cases our manufacturers have made no effort to develop special forms of apparatus of the highest grade in which great refinement is necessary, and for which there is only a very small demand from universities and research institutions. Much of such apparatus has been imported from Europe, where small but successful businesses have been built on just such work. Of course, the highly-skilled labor available abroad at relatively low wages has been an important consideration in this.

The alloy manganin, which is of fundamental importance in

most precision apparatus used in electrical measurements, was developed in America, but has heretofore been imported from abroad. It is to be hoped that American makers will market this alloy as well as others of similar characteristics in sufficiently good and uniform quality to meet the requirements of the manufacturers of precision apparatus. There is also an unfilled need for certain highly-specialized materials used in instrument manufacture, such as very fine wires, and small circular levels.

In comparing American and foreign-made instruments, it may be noted that the preferences of the user, which may be very different in different countries, have had an important influence on design. Americans often prefer to sacrifice somewhat in accuracy to obtain convenience and compactness. For example, certain foreign portable photometers are capable of greater accuracy than are American instruments, but the latter are much more compact and convenient to use, and their accuracy is sufficient to make them really more efficient in the work for which they are intended than are the foreign instruments.

It is interesting to note that two American manufacturers are producing galvanometers which are decidedly superior to any made abroad. The very highest grades of ammeters, voltmeters and wattmeters are available in American types. Very inexpensive direct current instruments are now made in large quantities, particularly for automobile service. American manufacturers have not, however, produced alternating current instruments in such inexpensive models as have the German and French makers. Hot-wire instruments for radio work were formerly imported, but are now largely supplied by American makers.

Thermometers and pyrometers: Nearly every type of thermometer used for laboratory or industrial purposes is now made by American manufacturers, such as clinical, calorimetric, Beckmann, low temperature, high temperature (1000° F.: 500° C.), and various types of industrial thermometers. Practically the only exceptions are thermometers of special types, of very limited use, such as deep-sea thermometers, liquid pentane-in-glass thermometers for use down to very low temperature (— 400° F.: — 240° C.), and primary standard thermometers. Industrial thermometers, sometimes called mechanical thermometers, are

mercurial thermometers provided with special mountings to adapt them to special applications in the industries, *e.g.*, for galvanizing baths, annealing ovens, distillation apparatus, etc. In this field of thermometry, American manufacturers have taken the foremost position and are exporting their product even to the European countries.

It was formerly necessary to import thermometric glasses; an American firm has now placed on the market special thermometric glasses that are in every respect as satisfactory as the well-known Jena normal and borosilicate glasses. Quite recently this firm has developed and placed on the market a new glass having a very low coefficient of expansion, which adapts it to a wide variety of heating requirements.

In the development of pyrometers, a very marked progress has been made in late years. Until quite recently we were almost entirely dependent on the product of European instrument makers for all high temperature instruments. Today, practically all types of pyrometers, thermo-electric, electrical resistance, optical, and radiation, are being produced by American firms. New instruments, now in development, which will mark a noticeable advance will soon be placed on the market. Several new and very active firms have been experimenting in the past three years and others have enlarged their scope and models.

We are still dependent, to some extent at least, on the products of European platinum refiners for the platinum and the platinum-rhodium wires used in thermo-electric pyrometers. It is much to be hoped that some of our platinum refiners will place on the market thermo-couples which although purchased at widely different times will yet be reproducible in their temperature scales to within 5° to 10° C.

Along with the developments in thermometry and pyrometry, there has been notable progress in the development of other instruments required in heat and temperature work, such as special resistance bridges and resistance thermometers used in calorimetric work, recording instruments for use with thermo-electric and resistance thermometers, instruments for detecting and for recording the critical points of steels, electric furnaces and ovens, bomb and other special types of calorimeters, gas calorimeters of the flow type, etc. All of these instruments have successfully

met the most exacting requirements of the laboratory and of the works.

In the recent developments, which have been briefly referred to above, the Bureau has often worked in close co-operation with the manufacturer, and has thus often been able to render valuable assistance and also has been in a position to control, in a measure, the accuracy of these products.

Optical glass and optical instruments: The chief factor in the manufacture of fine optical instruments is the production of suitable glass for lenses and prisms. A well-known European maker through long years of experience and thorough investigation has developed glasses adapted to various special needs. It is hardly to be expected that such results can be duplicated in a day, any more than a dye-stuff industry can be improvised, but it is gratifying to note that four or five American firms are attacking the problem of optical glass manufacture with marked success. The Bureau of Standards is also taking up the question in its broader aspects and hopes to be able to contribute to our growing independence of the foreign supply. There are few optical instruments not being made here today. We are making our own microscopes, spectroscopes, engineering instruments and binoculars, and are even exporting some of these articles. Perhaps the greatest need of this industry is the development of a body of highly skilled workmen.

Metals: America's rich endowment of minerals and her advanced position in the metallurgical art are matters of common knowledge. It would be impossible here to attempt to record the progress in this great industry, but it will not be out of place to mention several developments that may properly be considered within the scope of this review; for metals frequently form both the tool of the scientist and the subject matter of his investigations. Platinum is one of the most indispensable laboratory materials and American producers are making every effort to increase the supply. Notable quantities are being obtained from the copper refineries. For the purpose of determining and thus indirectly maintaining the quality of platinum ware, a method of testing devised at the Bureau of Standards has proved of great value. The method consists briefly in determining the thermo-electric

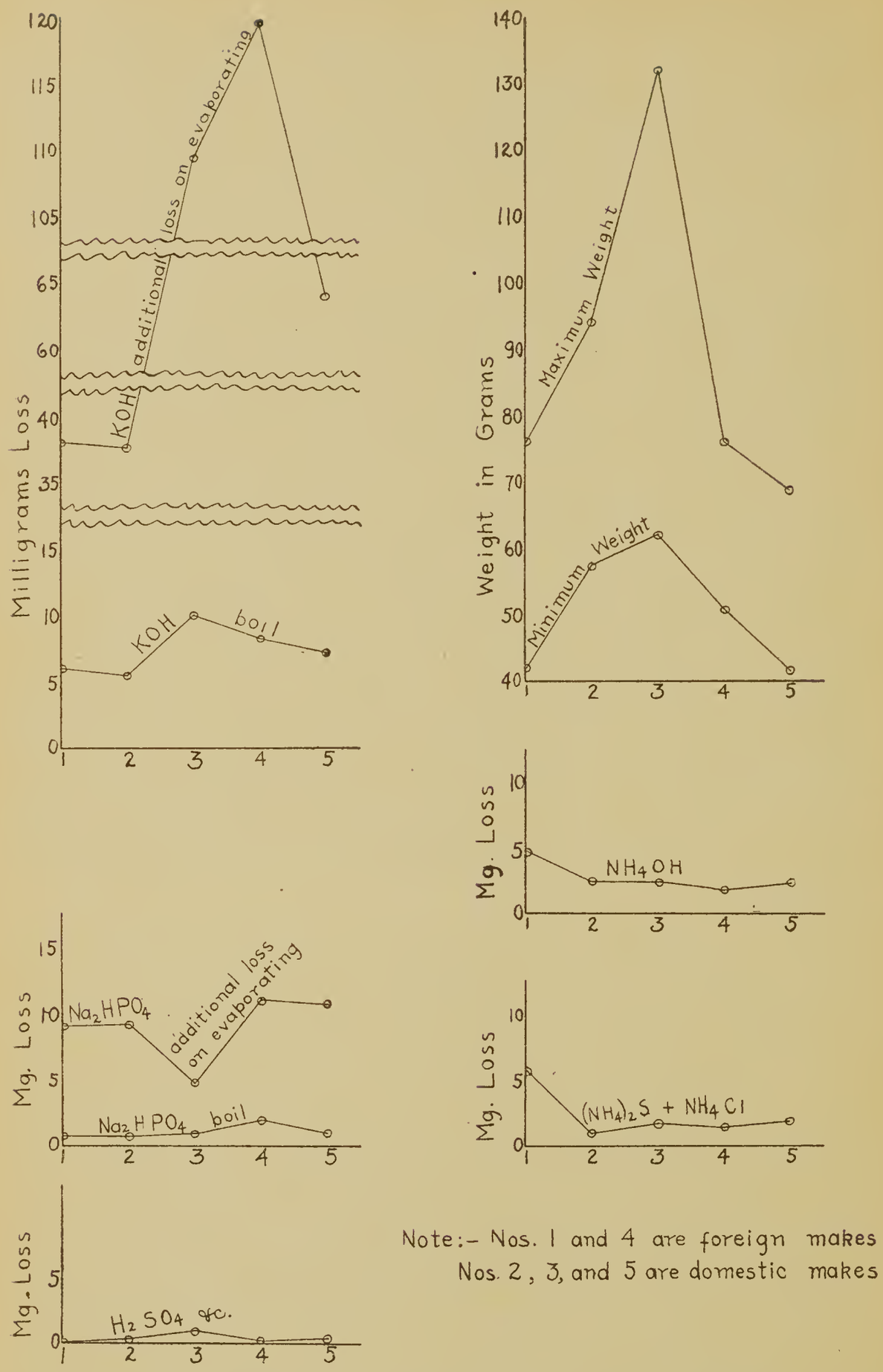

FIG. 1. Comparative tests of five qualities of glass beakers, for equal times, with reagent indicated.

force of the article to be tested against known pure platinum and then reading from a curve the corresponding rhodium or iridium content. In this way it is possible to determine with accuracy the total amount of impurity and to predict the loss in weight on heating, without in any way injuring the article.

As material for investigations the Bureau of Standards is at the present time greatly interested in the pure metals. Through the development and extension of electrolytic refining methods, American companies are now producing in considerable bulk the purest copper, aluminum, zinc, tin, lead, nickel, and cobalt. By melting point and other physical tests these metals have proved equal in quality for scientific work to the small samples formerly imported. In the case of the commonest metal, iron, it was found impossible to procure on the market a product of sufficient purity to form the basis of a projected study of this metal and its important alloys. The preparation was accordingly undertaken at the Bureau. A metal containing only three or four hundredths percent of impurities has been obtained in a form suitable for the determination of various physical constants.

Chemical glassware: Since it appeared that this country would soon be thrown entirely on its own resources for chemical glassware, a series of comparative tests of two foreign and three domestic makes has been carried out at the Bureau. As the details of these tests now in progress are to be published later, it will suffice here to present the results in the form of curves (Fig. 1) and to call attention to the excellent manner in which the American wares (2, 3, and 5) compare with the foreign products (1 and 4) as regards resistance to attack by various reagents. On treatment with water, with potassium carbonate, and with sodium carbonate, foreign glass No. 1 proved markedly inferior to the other four. On boiling with caustic alkalies the differences in behavior of the five makes are not significant, while on evaporating with such solutions all the glasses suffer such great losses that this treatment must be considered inadmissible. With ammonia, ammonium sulphide, and ammonium chloride, and a mixture of strong acids, all the makes behaved excellently, No. 1 showing a somewhat greater loss than the others with ammoniacal solutions. It may be concluded in general from the data obtained that the prob-

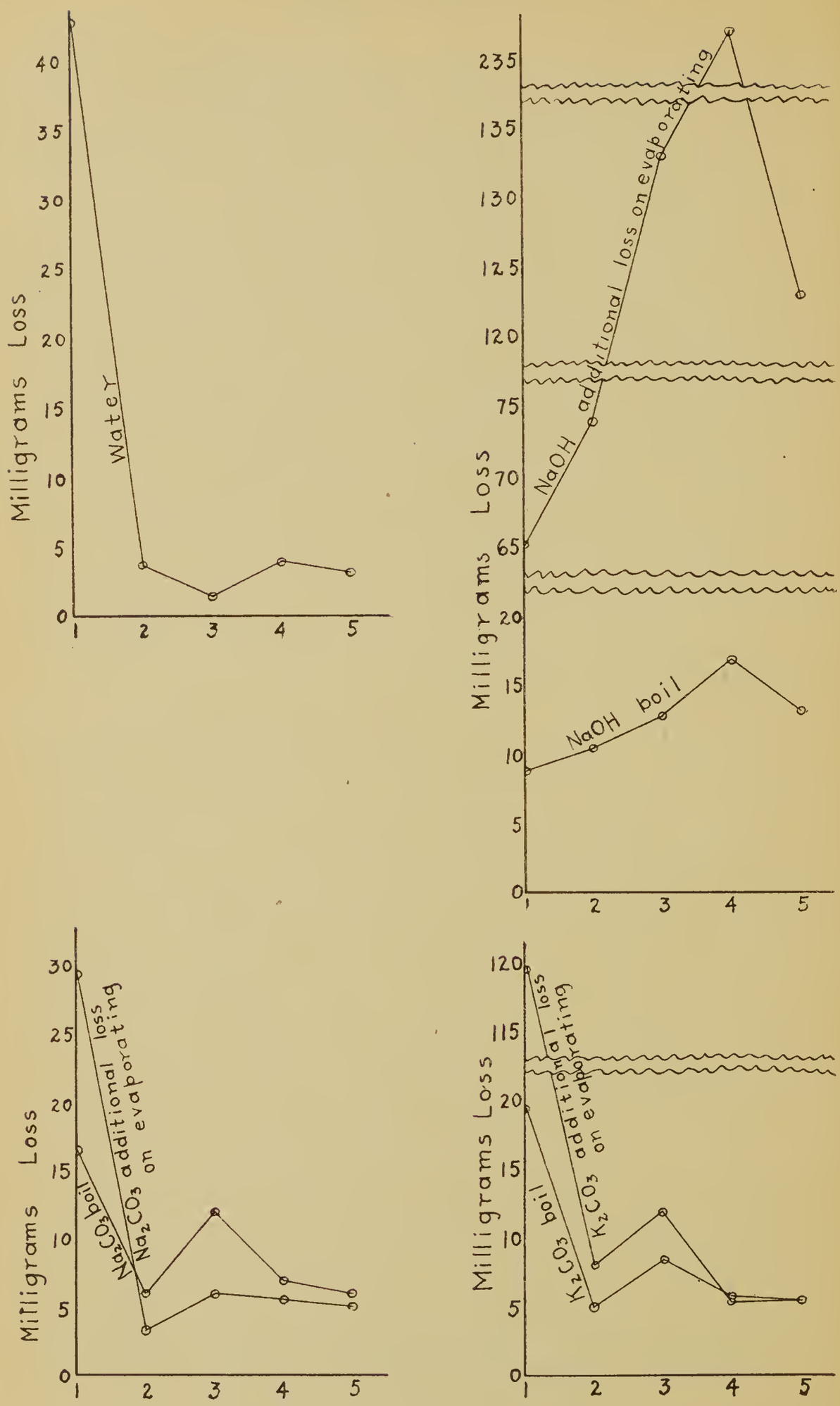

FIG. 2. Continuation of data from Fig. 1.

lem of making chemical glassware in America has been satisfactorily solved.

Kaolin Purification: In work done at the Bureau of Standards and elsewhere it has been shown that clays respond to colloidal reactions, and that caustic soda affords the best means of deflocculating most clays, that is, bringing about a greater dispersion by breaking up the larger particles into finer ones. In this manner the coarser, granular impurities of clay can be readily separated from the fine-grained clay substance proper, since the latter is kept in suspension. The principles underlying the refining of kaolins and other clays, as well as the effect of alkalies in the so-called casting process have been brought out in two contributions of the Bureau[2]. The process outlined has been installed in a plant in eastern Pennsylvania under the direction of the Ceramic Section and with excellent results.

Porcelains: A comprehensive study has been made of the various types of porcelain, both from the theoretical and the practical standpoint. It has been found possible to show clearly by means of petrographic examination what takes place in the vitrification of a porcelain and to differentiate between the several types of domestic and foreign porcelains. The temperature requirements in burning have likewise been established.[3] Simultaneously a number of hard porcelain compositions have been worked out which have been freely communicated to manufacturers interested in this work.

Owing to the impossibility of securing the refractory Marquardt porcelain used for pyrometer tubes, etc., work was done in this connection. A very satisfactory body and glaze have been developed, the compositions of which have been made public. At the same time the ceramic section has co-operated with one firm and assisted in the installation of a plant for the manufacture of this type of porcelain.

Plastic Bond Clays: The failure of the supply of the European plastic bond clays used in the manufacture of glass pots, graphite crucibles, etc., has made it desirable to establish clearly the physical properties of the imported materials in order to make possible a comparison with domestic clays which are available. For this

[2] Bureau of Standards, Technologic Papers Nos. 23 and 51.
[3] Bureau of Standards, Technologic Paper No. 80.

reason, five clays—four German and one French—were examined and tested.[4] From the results obtained, tentative specifications governing this type of clays have been suggested. It has been found that there is no reason why domestic clays should not be used to replace the foreign materials, but the fact is emphasized that not single clays but mixtures of two or three domestic materials should be employed. By proceeding in this manner, satisfactory industrial results should be obtained, superior in fact to those with the use of the imported clays, since the latter possess certain defects which can be overcome. At the present time at least six American deposits of excellent bond clays are available. Considerable co-operative work has been done by the Bureau with manufacturers interested in the use of these materials.

General Refractories: Considerable work is being done by the clay-products section in assisting in the working out of methods of testing and specifications for the different classes of refractories. It co-operates rather extensively with such associations as the American Gas Institute, The American Society for Testing Materials, and the Refractories Manufacturers Association. The results obtained in connection with the work on the ability of clay refractories to resist load conditions at furnace temperatures[5] have been generally confirmed. Some attention is paid also to the development of special refractories such as the spinels, zirconia, and other substances. An elaborate study of silica refractories is under way.

Use of the metric system: It would not be fitting to close this survey without some reference to an important step of progress brought about by the war. The growth of our trade with Latin America is forcing many manufacturers to adopt the metric system for their export business, and they are learning to think of grams and millimeters without an attack of mental prostration. The situation is well covered in Senate Document No. 241, 64th Congress, 1st Session, a report on the "Metric System in Export Trade" by the Director of the Bureau of Standards. The modes of use of that system are grouped as follows:

(a) Complete use of metric system in designing, making and selling.

[4] Bureau of Standards, Technologic Paper No. 79.
[5] Bureau of Standards, Technologic Paper No. 7.

(b) Price listing in metric equivalents (to enable the foreign buyer to understand quantities and prices).

(c) Packing products in units of metric size.

(d) Labeling metric equivalents on the unit packages, the contents of which may be put up in customary units.

(e) Stenciling shipping cases for export with the quantities in metric units to meet the customs requirements in metric countries.

(f) Filling metric orders with the regular-sized packages or products, merely billing in metric terms to enable the buyer to check price.

It is now possible to get all sorts of rules and gauges, taps, drills, and other tools in metric as well as ordinary units. Perhaps the greatest benefit of the adoption of the metric system in export trade will be the reflex effect on the domestic market. Many metric products have been found available for home use, and we may look forward hopefully to the day when we shall have advanced as far as China in the adoption of a scientific system of weights and measures.

In conclusion, the author wishes to call attention to the fact that this paper is essentially a compilation, and to express his thanks to the many members of the Bureau staff who have contributed the information on which it is based. He is especially indebted to Mr. P. H. Walker for the data on chemical glassware, and to Messrs. P. G. Agnew, C. W. Waidner, and A. V. Bleininger, who have written the sections on electrical instruments, thermometers and pyrometers, and ceramics, respectively.

L. E. Saunders: The ideas brought out by the two previous speakers will be open for discussion after I have endeavored to present the information which has been secured through inquiry amongst users of manufactured articles, and amongst the manufacturers, themselves.

A proper beginning for such a discussion in the electrochemical industry will be the matter of carbon electrodes. Before the European war started we cannot deny the fact that a large quantity was imported from various European countries. The number of replies to our inquiries from users has been extremely gratifying.

Every user of whom we have inquired has stated that it is possible to secure in this country large electrodes of as good a quality as was purchased abroad two years ago. There is, of course, a possible erroneous conclusion here. It has been brought to our attention that progress may have been made by the European manufacturers and as great an improvement may have resulted as has been experienced in this country. One user states that when the war started there were no carbons of large size to be compared with those of European manufacture. Another user states that some of our carbon manufacturers have been successful in improvement and others are not doing as well as they did when severe competition had to be met. Still another user says that they are unable to furnish any testimony in this respect, as they have used nothing but American made electrodes. Undoubtedly, these latter people would come in the class mentioned before, as favoring a slogan "Made in America," and the purchase of articles bearing that slogan, whatever their quality might be.

Some users have gone into detail in the matter of carbon electrodes, and have stated: First, that the perfection of manufacture is very high in our American made carbons. Second, that the resistivity is even less than the best of European carbons and that annealing has been so perfectly done that breakage almost never occurs. This user is, of course, an enthusiast, for those of us who use carbon electrodes realize the Utopian nature of the last statement.

One of the complaints that has been made by a user is that the price of European electrodes delivered was about forty percent less than the cost of the best American electrodes during the past year, and that there is no such difference in quality as to warrant such a difference in price. It is, perhaps, needless to point out that we do not know what the cost of European electrodes might now be delivered in the United States, but it is safe to say that it would not be the price at which they were sold two years ago, and there is at least a question whether such a difference in price will occur again when the manufacturers meet in competition.

I am very sorry to say that so far no manufacturer of carbon electrodes has sent us any testimony of his own. Perhaps it is fortunate that the testimony of the user has been so favorable, otherwise a serious indictment against the manufacturer would

have to stand for the reason that no defense by the manufacturer has been made.

I turn now to the use of electrodes in the electrolytic field, and here, again, I am obliged to say that there has been no adverse criticism of American made articles, in fact, they have so uniformly favored a single manufacturer, that it becomes embarrassing to make any statement. In only one instance has testimony come in where a carbon electrode has been used in wet electrolytic work, and even in this case it is reported that those purchased in this country were preferable to those secured from abroad. All our other testimony on this subject states that graphite electrodes are used. Inasmuch as this is so, I dare say the manufacturer has not considered it necessary to make any statement in reply.

The next subject on our list, and one which necessarily is of a restricted nature, concerns the metal platinum. One of our most prominent professors of electrochemistry has stated in a letter that no American made platinum makes any pretence of being good. Other users state that platinum vessels have been supplied by American manufacturers containing so much iron and iridium that they cannot be used for accurate analytical work and are attacked when used on a large scale in other ways. This is a serious arraignment of American made articles. We gave to the manufacturers every opportunity to meet objections of this character, in fact, we even furnished the specific criticism in one case in the hope that we might produce something in reply that would have a little ginger in it. However, we were unsuccessful. The calm and confident statement was made that competition of years had been successfully met by American made articles, and that there has been no demand for quality of products that the American manufacturer has been unable to supply. We hope this will be a subject for proper discussion, and that a suitable defense made before this session is over. Since writing this, the following letter has been received:

"In December, 1910, the Division of Industrial Chemists and Chemical Engineers of the American Chemical Society established a Committee to study the question of the quality of platinum ware and report specifications for the benefit of the consumer. This Committee's report was published in The Journal of Industrial and Engineering Chemistry in September, 1911, and its conclusion, abstracted from page 690, was as follows:

'It has been shown that ware of foreign make can be had against which nothing can be brought on the score of iron or other base metal content

and in which the loss caused by strong blasting seems to be solely of platinum itself and to be entirely negligible, for all ordinary purposes, up to at least 1100 degrees.

'It appears also that American-refined platinum ware can be had of nearly if not quite as good quality and there does not seem to be any reason to think that its quality cannot be still further improved if there is a call for it to be done.'

"The above report seems to be a sufficient answer to the broad charge of your correspondents that 'American platinum makes no pretense of being good.'

"While it is true that the quality of platinum ware is dependent upon the specific demand and price paid for guaranteed composition and physical properties, there is no question but that platinum ware equal in every respect to the foreign make was an obtainable product in this country long prior to the present war."

We have endeavored to secure from users statements on the situation with regard to fine chemicals. We have had no criticism in reply to our letters. In conversation, however, I have been told that it has been the experience of several users of potash salts of high purity that they cannot be obtained at the present time. A user has stated that this was so for a considerable period, but is being remedied. It is also stated that sodium salts, in many cases, are being substituted for potash salts formerly used in an analytical way.

In all cases of fine chemicals the manufacturer has declined to furnish us his standpoint, and it is our hope that there are representatives present who can give us some really tangible information.

I shall briefly mention, only in passing, the subject of ferro-alloys. The quality of the products of this character made in this country has always been, almost from the time of the beginning of the industry, of the highest possible character. Unless we, here at this meeting today, hear something to the contrary from some one with experience, I think it can be safely said that so far as the article manufactured is concerned, no hardship has been suffered with respect to ferro-alloys. I do not refer now to the question of securing raw materials and ores which enter into their manufacture, but simply to the skill and art of the manufacture itself.

I mention in the same manner the subject of electric steel. The testimony at hand has not been large, and it may be that something has escaped in the investigation. I know that special steels have been made abroad which during the early period of the short-

age here could not be duplicated. This, I believe, is rapidly being overcome and I feel safe in saying, subject to correction at this meeting, that electric steel, of all qualities, made in this country has never been excelled.

One of the other subjects which has been assigned to me by the directors in the course of our discussions on the whole subject is the metal, aluminum. Inasmuch as there is but one manufacturer, and inasmuch as the statistics show that very little aluminum has ever been imported, it seems that no statement pro or con can be made without taking sides and becoming unneutral. If any one during the discussion decides to take up such a position, I am sure no one will object.

Perhaps the matter on which we have received the greatest amount of testimony is in connection with the chemical glass industry. The users are, to a considerable extent, pessimistic. Quoting from a well-known college professor, the statement is made: "American glassware is very much inferior in workmanship, in most cases in quality, besides costing anywhere from two to five times as much." Another large user states that we cannot make a suitable glass without potassium and the proper silicates, nor without the proper clay materials for the pots, and these are not obtainable in this country. The same user is extremely pessimistic about remedying this situation. He states that in many cases abroad the making of fine glassware is a family affair, and the son follows in the father's footsteps, these men not being willing to leave their country, and when they do come they can command better wages than the industry can afford to pay. Another user states that, compared with Jena glass, certain American made glasses are more resistant to the action of both acids and alkalies, especially the latter, for example: When boiled in ten percent sodium hydroxide solution, its loss in weight was less than sixty percent of that sustained by Jena glass under the same conditions. Its resistance to shock and to sudden changes of temperature seems to be somewhat better than certain imported glassware. Another user states that resistance to sulphuric acid was higher in the case of American glass than of the best imported glass. Still another user placed test tubes filled with distilled water in an autoclave and kept them there for 45 minutes at 12 pounds pressure. No trace of alkaline or acid substances was

found in the water with a large number of indicators. Very few foreign glasses, it is stated, can withstand this test. On the other hand, one user states that he is unwilling to publish the data he has obtained on both glass and porcelain for patriotic reasons. This statement certainly should draw out something from those present here.

We have been furnished with a large amount of data by manufacturers and all are agreed that our greatest difficulties at present are with light-blown glassware. While workers from abroad have been brought to this country, the demands are so heavy with the European supply cut off, that hardly a beginning has been made in meeting the demand. Wages for this class of labor have gone up on account of the great demand, so that prices have also increased. It may be said, however, that this kind of ware can be produced in this country, and it is simply a question of quantity rather than quality that is troubling the user. One manufacturer of glassware has stated that the linear thermal expansion has been reduced in the glass of his manufacture to just about half that of the imported glassware. He states that fewer constituents are contained in the glass, which may contaminate solutions in analytical and other delicate chemical work. For instance, this glass is free from the elements calcium, magnesium and zinc. Tests of this glassware for solubility in distilled water showed a very much smaller solubility than with the German glassware (kind not stated). This same manufacturer gives results of tests in regard to breakage on sudden cooling. The beakers are filled with paraffine, and heated to a desired point, then immersed in water at 15° C. The temperature reached before fracture averages 253° C. No data is given with reference to beakers of foreign manufacture. Tests were also conducted in the way of resistance to fracture by dropping. The beakers are dropped from varying heights onto a 2-inch (5 cm.) pine plank. The average height which these beakers withstood was 30.7 inches (77 cm.). A large number did not break at 36 inches (90 cm.), and were not carried further. These are tests which apparently are used to give a favorable comparison of American glassware against that of German make.

Still another manufacturer gives data on glass baking dishes which, to the writer's knowledge, were never imported from

abroad. Therefore, the data is not exactly in order in this discussion.

Another manufacturer states that the element potassium has been eliminated from certain glasses, resulting in the saving of a large amount of potassium carbonate, and that the glasses in many respects are superior to the old.

Another development is in optical glass. It is stated that a glass has been developed which is faintly yellowish in color and which absorbs all ultra-violet rays and therefore is especially useful in the manufacture of glasses for electric furnace work.

Another manufacturer has stated that he has been able to manufacture a very limited line of glassware for laboratory use, but has been unable to extend his line on account of manufacturing conditions.

This testimony, both by the user and the manufacturer, seems to be overwhelmingly in favor of the conclusion that American made glassware can be secured which excels in numerous properties that which has been imported from abroad. The criticism in regard to price seems to me an improper one and the subject would be more properly discussed when competition again occurs.

Our next subject, and one which is of great importance, is that of chemical porcelain. Here we have again had much testimony, principally from the manufacturer. That there is a prejudice, however, may be seen in the statement of a prominent member of this Society, as follows: "I certainly was surprised at the cracking of a small porcelain crucible I was heating. I could not find the crossed swords on the bottom. It probably would have had 'Made in America' on it if marked at all." By the testimony which follows it would seem that even so high a recommendation as the crossed swords is not the *ne plus ultra* which this testifier would have us think. One man who states that he has used American made porcelain in four weeks of summer school, says that he has lost all idea of ever being able to secure good American porcelain. Turning from this pessimist for a moment, it is good to find such testimony as the following:

Heating and cooling test, American made porcelain against Royal Berlin, number cracked or crazed: In the case of Royal Berlin one; American make none. The test consisted in heating the sample to 1700° F. and then removing with a pair of steel

tongs and tossing upon a steel plate in a draft. Next test solubility in 20 percent sodium hydroxide boiling for 6 hours: American made porcelain 1.5 percent; Royal Berlin, 1.8 percent. Next test effect of ferric oxide ignition on glaze: American make gained in weight 0.001 percent; Royal Berlin 0.006 percent.

Numerous other tests are reported, but comparison not being given, they are not quoted.

Certainly, no pessimism is in order as the result of such tests. The greatest criticism that has been received on these artcles is the long time it takes to secure them, and surely no one can say that this can refer to the quality of the articles. On the other hand, another user has stated that his bills for both glassware and porcelain have been cut in two by the use of American made ware as compared to that of foreign make.

The question of chemical stone ware has received little attention, as we have been able to gather no testimony to speak of. One user states that the American made stone ware depends for its resistant qualities entirely on the glaze. When this is removed through accidental or other means, the body of the ware is very easily attacked by the solutions which are handled in this grade of material. Some testimony on this point at this meeting would be interesting.

This is but a meager introduction to this subject. We undoubtedly shall hear much about these things both from the user's and the manufacturer's standpoint.

We have also had a great deal of testimony in connection with dye stuffs, organic chemicals of all sorts, and some other references which do not seem to have to do particularly with the electrochemical industry. We are therefore not giving them much space in this review.

In the case of electrical instruments we believe that the situation has not changed since the war, as American made instruments, by common consent, are the best in the world. Chemical balances are made with great success in this country; machinery used in the electrochemical industry has been nearly always secured here; microphotographic apparatus made here, it is stated, is far ahead of anything made in Europe. Articles like filter paper have been long made of high quality; microscopes of American manufacture cannot be beaten. Some other instruments which have been made abroad are being worked on now in this country.

DISCUSSION.

A. T. HINCKLEY: The opinion has been expressed that large electrodes were among the products which before the war came exclusively from abroad, but are now made in America. This is hardly a correct statement of the case, as large electrodes were made in America before the war and were used successfully in many electrochemical and metallurgical industries. It is true that many electrodes were imported, but that was quite natural when one considers that many of the furnaces and processes were either originated abroad or were in charge of men whose experience has been gained abroad. It is natural that they should have preferred the make of electrodes with which they were familiar.

The war made it necessary for those users to turn to electrodes made in America, and they found in general that the American-made goods were equal, and in many cases superior, to those which they had been obtaining from abroad. Even before the war, the tide was not entirely from the East to the West, but the American manufacturer had some of the foreign trade, and that foreign trade has increased.

I believe that the war has caused few changes, if any, in the method of making large electrodes in this country, and that the growth of the business from a technical standpoint, not from the volume of business, has been only such as would result in any equal number of years under normal conditions.

W. C. MOORE: In a "Made in America" symposium, a brief statement as to the part played by the carbon manufacturers in making this country independent of foreign nations with respect to brushes, arc lamp electrodes and other carbon products may not be out of place.

As is well known, generator and motor brushes are made in a wide variety of sizes, shapes and composition to meet the various classes of service. For many years the user of electrical machinery in this country has had at his command excellent American brushes for all purposes where such brushes are used; in fact, certain brushes made in this country for railway and high-speed stationary work have long been superior with respect to life, coefficient of friction and freedom from chipping, etc., to any

others on the market. A certain company making electrical machinery had been in the habit of using foreign brushes, but recently learning through one of their customers of the excellence of American-made brushes, sent in a large order. This is but one of many instances. The situation with respect to arc carbons for moving picture projection is very interesting. Some time before the outbreak of the European war, a "projector" carbon was developed in this country, which gives higher candlepower than any foreign carbon made. This carbon was introduced at first to a limited circle of users, who found it so satisfactory that even before the war started the demand could not be supplied. By almost herculean efforts, however, the great demand for projectors, which became quite acute after the beginning of the war, was met; and in addition further development work was carried right along so that today there are on the market improved types of carbons which are far better than any ever made before. One of the improvements introduced in the last year is a small metal-coated negative, which steadies the direct current arc and eliminates the shading effect of a large negative. There are today theaters which, starting operations late in 1913, have never used any but American carbons; many others, using them in the last two years for the first time, have been so pleasantly surprised at the quality and service that they will probably never order another foreign carbon.

For a great many years users of open and enclosed arc lamps have used American-made carbons almost exclusively. With respect to flame arc lamps, it is generally known that there are two general types; the inclined trim lamp, in which the arc burns under open arc conditions; and the vertical trim lamp in which the arc burns in a tightly closed space. The mechanical, electrical and luminous superiority of American-made carbons for the first type of lamp has long been a matter of common knowledge; as an example may be cited the use in these long carbons of zinc wire *soldered* to the carbon; in this way the dark deposit due to the brass and the loose contact due to simply bending the wire over the end of carbon, both features of foreign carbons, are avoided.

The "vertical trim" lamps use solid, impregnated carbons. For a year before the outbreak of the present war the largest user

of white flame carbons in the United States was using an American product, which is superior to the German-made article in freedom from flicker, freedom from slag and in life. This does not seem to have been well known, but the following statement, recently made by a prominent electrical manufacturing concern, seems to show that at last it is realized that we no longer need go abroad for arc supplies. "The flame carbon arc lamp within the past year has become practically independent of the foreign manufacturers of carbons, excellent results having been obtained with domestic carbons. This points to a retention and noticeable expansion of this business in the near future." (Electrical Review and Western Electrician, Sept. 2, 1916, **69**, 401.)

Any statement about arc carbons is incomplete without a reference to "photographic carbons." These are used in arc lamps for photo-engraving, blue printing, photography, etc. This use of the arc has been growing steadily until today almost a million carbons per year are now sold for such purposes. In passing, it should be emphasized that most of these uses are American developments.

Other carbon products which we do not have to depend upon outsiders to furnish are back plates, granular and globular carbon for telephone work; contacts, packing rings, plungers, and plates for carbon plate resistances. Interesting developments of the latter are the corrugated plates, which increase the power-dissipating capacity of a flat plate; and the staggered plate rheostat which has a greater range of resistance than the corrugated plate. While writing this note, a glowing tribute as to the ease of regulation of a corrugated plate rheostat was received from a St. Louis manufacturer.

A point which should be emphasized is this: development work in carbon products has been carried on in this country for many years. This work is being followed up more intensely and thoroughly today than ever before, for we realize that only by such development is continued progress possible, and it is absolutely essential that progress be made in order to have this country remain independent in this and other lines.

J. W. Beckman: It may be of interest in this connection to let you know that even on the Pacific Coast they have started to make electrode carbons. We have there a raw material which is

different from any raw material existing any place else. It is lamp black obtained as a by-product from cracking oils, and there is a company manufacturing today arc carbons from this material which are supplanting, to a great extent, other arc carbons.

T. H. SCHOEPF: Dr. Moore spoke of the American-made carbon brush for electrical machinery. Up to four years ago, we had no American-made brushes which were equal to the foreign made. Today, American manufacturers of brushes have equaled the foreign made brushes which we were getting prior to the war. Whether there has been an advance in the quality in the European brush since that time I do not know. I think that American manufacturers are making carbon brushes equal to any now made in the world. No one class of brush will answer, however, for all classes of electrical machinery. The same brush may not work with the same degree of success on two different electrical machines.

E. A. COLBY: I wish to speak on the subject of platinum, since the chairman of this Committee has quoted a well-known professor as saying that "America makes no pretense of making good platinum." It seemed to me that the best answer to make to such a statement was to quote from a report of the Committee of Experts appointed by the American Chemical Society, which report has been read by the chairman of your Committee. If anything can be added to that report, it would be simply to this effect —that, as a matter of fact, American manufacturers of platinum can make, and do make, and have been making platinum of high quality for many years past. It is not a question of the ability to make, but of the willingness on the part of users of platinum to pay for platinum of specified quality. Platinum ware, as you know, must have certain qualities which are distinct from platinum used in many other operations, and the report of the Committee of the American Chemical Society on platinum ware discloses, I think for the first time to the general public, the deleterious effects of a large iridium content, its effect being a serious loss of weight in service. There was submitted to the Committee at the same time, ware made of an alloy of platinum and rhodium. The result of that investigation showed a loss in weight much less than platinum containing iridium, or even than pure platinum. As a

matter of fact, platinum of any degree of purity can be produced, and is made today, for laboratory ware, containing as little as 0.05 percent of rhodium, or, in exceptional cases, 0.006 percent. If desired, chemically pure platinum is produced and supplied.

I understood the gentleman representing the Bureau of Standards stated in his paper that "Platinum and rhodium are not obtainable in this country for thermo-couple work."

EDWARD SCHRAMM: I did not say it was not obtainable, but the statement was made that it was not equal in quality to a certain foreign ware for fine thermo-couple work. By this I mean that couples purchased at different times have not in the past shown the same uniformity and reproducibility of thermo-electromotive force.

E. A. COLBY: Representing one manufacturer of platinum, I would be glad to submit samples of materials which we are making daily for use in conjunction with the instruments supplied with the Heraeus thermo-couples.

EDWARD SCHRAMM: I refer you to Dr. Waidner, Chief of the Heat Division of the Bureau, as he is responsible for the statement made. Dr. Waidner will be glad to test any samples submitted.

E. A. COLBY: Electrochemists demand platinum of many forms and compositions, greater in variety than the ordinary laboratory chemist. If it is feasible for this Society to appoint a Committee of Electrochemists to investigate the quality of platinum and its alloys, the manufacturers will be glad to submit samples or conduct any series of investigations under the Committee's supervision to prove the fact, as they believe, that the American product is equal to that to be obtained anywhere in the world.

J. W. BECKMAN: The correspondent whose letters Mr. Saunders read states that he would be unpatriotic if he said what he thought of American-made porcelain ware.

Did not this correspondent show an unpatriotic attitude by not being willing to criticise American-made products? Would it not have been true patriotism if this correspondent had given his full and free opinion of the product, thereby helping the manufacturer to improve his product and thus a home industry would have been helped to compete with a foreign-made product.

L. E. SAUNDERS: It occurred to me after hearing some of this discussion, that the well-known member, a college professor, from whom I quoted extensively, has been suffering from a short pocketbook more than anything else. It would seem that if he were willing to pay the price he could get good platinum. The same professor referred to the glass situation, and the strongest part of the statement was that it cost from two to five times as much for the American-made as for the foreign-made glass. If he is willing to pay the price, he can apparently get as good things as he wants, perhaps that is the attitude of a good many college professors.

J. W. RICHARDS: That statement should not pass without the remark that the question of the same quality *at the same price* is the main question before us, and it is not a question whether you are willing to pay a higher price for the same or for better quality, but simply whether you can get the same quality for the same price.

F. C. FRARY: With regard to the references that have been made to the importations of glassware for university use, or industrial use—and this applies also to porcelain ware—I would like to point out one or two facts.

In the first place, buying glassware for two or three chemists in a laboratory doing routine work is very different from buying it for fifteen hundred students who do not know much about what they are doing or what they are trying to do. The matter of price obviously makes a great deal more difference to the university than it does to the industrial plant, while the matter of quality is often not nearly so important. The industrial plant may be anxious for the glassware to show low solubility, while the university, for many of its large classes, cares nothing about the solubility of the glassware, but is interested chiefly in breakage costs. That difference, I think, really calls for some difference in quality. Personally, I believe in using a fairly high quality of glassware for university work, but it is certainly a very different problem from that of supplying a technical laboratory, whose requirements and course of work can be much more accurately and satisfactorily estimated before hand.

C. G. FINK: This meeting this morning, on "Made in America," we of the New York Section consider the most important meeting of our Convention. The public in general has for years past considered the chemical products and apparatus made in Europe as superior to any of those made in our own country. It is this ingrained impression of the public which I hope we will be able to dispel and get rid of completely. As a result of the war, products have been brought to the attention of the public, products, some of which have been made here in America for many years, which are not only as good as, but even better than, products made abroad. We never knew it, because we never took the time and trouble to find out.

Take for example the case of plate glass used by our better-class picture framers. These men have always believed the only really good glass to be the Belgian glass, and it is only within the past year that they have become convinced that American plate is not only cheaper but decidedly better than the Belgian brand. Numerous other instances could be cited.

G. A. ROUSH: As Dr. Fink says, there seems to be a general impression that a thing to be superior must be foreign-made. I think so far as the student who takes a chemical education in a college is concerned, he gets that sort of an impression from the fact that the college material is practically entirely imported duty free from European countries, mainly Germany, and without stopping to analyze the exact status of the situation, he comes to the general conclusion that the material is obtained from abroad because it is better than anything we can get here, and not because of the actual reason that there is no duty on such imports by educational institutions. If the same material were purchased in the open market for an industrial institution without the benefit of the tariff reduction, the probabilities are that material of equal quality could be obtained at approximately the same price, or possibly a slight increase.

J. W. RICHARDS: Mr. Saunders raised a question as to whether the aluminium made in this country was equal to or superior to that made abroad. I think there is practically no difference in the qualities of these two metals; the principal commercial difference in the past has been the duty of three cents a pound on the foreign metal.

Two years ago, one of our members, Mr. E. A. C. Smith, in describing the copper leaching process at Chuquicamata, Chile, showed us the magnetite electrodes which were then being made for him in Germany, and which were then ordered to the number of sixty thousand for the Chuquicamata plant.

When the war broke out they were unable to get these electrodes, and were thus put in a very bad hole. They considered all other sorts of materials, and finally conducted a number of experiments to make these electrodes themselves, not knowing exactly the technique of the manufacture in Germany. It should be a source of gratification to us to know that all of the magnetite electrodes which they are now using are being made by a process developed here in America for the company, partly by themselves and partly by others, and these are far superior in quality to those which were heretofore procured from Germany.

W. C. Moore: In my work I have recently been using a large number of ordinary 360° C. mercury-in-glass thermometers. They were not marked "Made in Germany," but I have always calibrated these thermometers before using them, and have found them anywhere from 3° to 6° off. In one case one was 6° high at zero, 32.4° and 100°. The scales were not anywhere near as close as they should be on such thermometers.

M. B. Smith: We have found an American-made thermometer which stands up very well, but these thermometers must be used in the manner in which they were calibrated by the maker, or due correction made for emergent stem.

On an ordinary 300° thermometer we frequently find 10° to 15° variation, where 5° or 10° of the stem only is immersed. On the other hand, if we immerse the whole stem, we find that the calibration is more nearly correct.

On 600° or 700° thermometers, we have often found as great an apparent error as 30° around a temperature of 650°, whereas if you immerse the stem completely you may not entirely do away with the apparent difference, but you will cut it down to a point where the correction is very easily made.

For that reason, we plot curves for each individual thermometer showing what the correction is all the way up the scale for a certain emergent stem.

W. C. MOORE: In the thermometer I had reference to, the reading was high instead of low. If the scale were all right, and no corrections made for the emergent stem, the readings would be lower, but these readings were 3° to 6° higher than the true temperature, so it was not a question of correcting for the emergent stem at all. I have forgotten the amount of emergence it showed at 100°; but at zero and at 32.4°, the whole stem was immersed. The readings were high, and not low.

W. H. WALKER: At the Massachusetts Institute of Technology we are very large users of the ordinary chemical apparatus, and while I am not very conversant with the details of our needs, however, in talking to our purchasing agent the other day as to the material we were receiving, his reply was one of distinct hopefulness for the future, in that we are now getting materials which are much better than we have had at any time during the last year.

It seems as if we must adopt a spirit of tolerance with reference to our American manufacturers if we ever hope to become independent of the European manufacturers of chemical supplies. We must give them time to acquire experience and arrive at the standards of excellence which the European manufacturers have taken years to reach. I think the whole atmosphere is one of promise, and if we are patient, as we can well afford to be, with our domestic manufacturers, we will in time reach that standard which we all hope and believe America can attain and maintain.

A. S. MCDANIEL: I think a remark about photographic developers might be of some interest to this audience. There is seemingly a very great lack of information about the quality of photographic developers. For instance, one shipment from a well-known manufacturer of something like 200 lbs. (98 kg.) of photographic developers contained less than an ounce (28 g.) of that particular chemical.

Another point I think might be of interest to the electrochemist is that in the early stages of the war we succeeded in bridging over a certain time by making certain developers electrochemically. That process is now being carried out practically, but the future of the process is not certain, it depends upon the market conditions, and it is very probable, to my mind, that the electrolytical process will not only prove as economical, but far more economical for that process, than the chemical method.

A. M. WILLIAMSON: One might gather from what has been said regarding chemical glassware and porcelain that the manufacture of these articles has been recently taken up in the United States. I think it is only fair to say that one concern has been manufacturing high-quality chemical glassware in this country fifteen years and their product had replaced Jena glassware in many large industrial laboratories years before the war cut off the foreign supply.

D. A. LYON: In the United States Bureau of Mines laboratories at Salt Lake City we find that the glassware and porcelain now being made and sold in this country is entirely satisfactory for our work. We are, however, having difficulty in finding suitable filter paper.

J. W. RICHARDS: My experience as an analytical chemist may be of a different nature from that of Dr. Lyon, but we abandoned the use of German papers some years ago, in our inorganic chemical laboratory.

WILLIAM BLUM: A subject which is not mentioned in the report of the Bureau of Standards illustrates, not a case of "Made in America," but something we have had in America for a long time, and which has not previously been made use of. The Utah deposits of ozokerite wax have been known for twenty-five years, but it was impossible to market the American material in competition with the Austrian and German product.

Now that the foreign supply is cut off, the American manufacturers have taken steps to put the American wax on the market; which fact will be of interest to electrochemists in connection with certain types of electrical insulation and electrical condensers.

M. B. SMITH: I believe that a few words are in order regarding thermometers. I have no intention to impugn the verity of the calibration carried on by our friend Mr. Moore. A curious fact is this—among all the thermometers we have tested we have yet to find one which has read too high, and for that reason we went after the question of the emergent stem correction.

We have proved, beyond any reasonable doubt whatever, that the stability of the glass itself has a great deal to do with the veracity of the thermometer, and we have found that all the

American-made thermometers which we have tested must be calibrated frequently.

F. C. FRARY: At least one manufacturer makes a thermometer calibrated for definite emergent stem, or one to three inches (2.5-7.5 cm.) immersion. This is more convenient than an ordinary thermometer, if you want to use it in that way.

ACHESON SMITH: Some things can be tested in the laboratory and some things can only be tested by watching them in actual service, and other things can only be adequately tested by watching their performance for years. Thermometers might be quickly tested in a simple way, while electrodes might have to be watched for a number of years to get anything that resembled a good average.

It seems to me, however, that the burden of proof rests upon the manufacturer to show whether his goods are of as high quality as something which is imported, and the thing I tried to emphasize in my remarks was the point that the manufacturer should make every possible effort to find out for himself, by all the tests that he can possibly think of—laboratory tests and in consultation with the customer and watching the goods in service, and in any other way that he knows of—the exact behavior of the goods. There really ought to be very little difference of opinion regarding the value of an article, between the user and the manufacturer thereof.

L. E. SAUNDERS: I for one do not like to buy things on a firm's reputation. I prefer to buy them and try them. Take the case of carbon electrodes: If I had been buying European electrodes and the supply were suddenly cut off, it seems to me that I could tell, not depending on the reputation of years of service of any particular make of carbon, in a comparatively short time what American-made electrodes were going to do. In fact, I know already what they are going to do, because I have tried them. We had some trouble, at one time, with electrodes "that cupped and peeled." Those times are past, and we have pretty good electrodes now. There is room for improvement in them, of course, but they are pretty good and I think the test that users can make, and have had an opportunity to make, year by year, ought to be pretty safe as a basis to decide on in the use of such articles.

The gathering together of the testimony presented here was not intended to be final in any way. As Mr. Smith has said, it was the idea to get the user and manufacturer together, and it seems we have done quite well at that.

R. C. Canby: I will say a word about bringing the user and manufacturer together. I was in Colorado in 1884 and we were using crucibles and scorifiers imported from Battersea, England. There was a firm in Denver making fire brick, and they experimented in making crucibles and scorifiers, and we tried these. At first they were unsatisfactory, but inside of a year, or possibly less than a year, they solved the problem, and we all know that American crucibles or scorifiers are universally used now in our Western country.

J. W. Richards: In connection with the question of refractories, there is still the problem before our American manufacturers to make plumbago or graphite crucibles which are equal to those made from foreign materials. At the present time crucibles have gone up in price 200 to 300 percent, and their quality has deteriorated in the same proportion. That has increased very greatly the cost of making crucible steel, and one of its incidental effects has been a great enlargement of opportunity for the electric furnace.

This is not primarily a question of manufacturing goods equal to foreign made goods, but it is a question of finding suitable American raw materials, and blending them so as to produce results that were obtained formerly with the imported materials. That is a large question, which the crucible makers have not at all satisfactorily solved.

Edward Schramm: In this connection it may not be amiss to call attention to the fact that many cases of failure of crucibles are due to improper handling by the user rather than to improper manufacture. A crucible properly handled will give good service.

J. W. Richards: It should be stated that people who have been making crucible steel from ten to thirty years have found they cannot possibly get more than one-third to one-half the life out of domestic-made crucibles at the present time as compared with two years ago.

ACHESON SMITH: Is it not a fact that the users of crucibles, owing to the shortage of the supply, have not been able to anneal them for as long a period as usual? Many users ran short eighteen months ago, and probably have since never been able to get ahead so as to give proper time for annealing. If the annealing period is shortened it would undoubtedly tend to shorten the life of the crucible in service.

J. W. RICHARDS: That may be the case, in some instances, but the larger difference is in the quality of the crucibles themselves.

ERNEST CHILD (*Communicated*): The most necessary laboratory articles from a commercial standpoint can be classified as follows:

(1) Glassware.
  (a) Moulded Glassware.
  (b) Blown Glassware from liquid glass.
  (c) Light Blown Glassware from tubing.
(2) Porcelain Ware.
(3) Metal and Wooden Ware.
(4) Filter Paper.
(5) Balances and Weights.
(6) Chemical Optical Instruments.

(1) (a and b). Before the war there was one concern only making goods in this line, comprising such articles as beakers, flasks, bottles, and so forth. Since the war, several concerns have engaged in the manufacture of these goods, with remarkable success in some cases, the beakers and flasks of one concern being superior in chemical stability, resistance to temperature, and mechanical stresses to best imported, which formerly held first place. It seems reasonably sure that several of these concerns will maintain their lines after hostilities cease, but as to how many, that is problematic, depending on tariff changes and whether or not duty free importation for educational institutions is resumed.

(1) (c). The light glass line comprising articles that are blown before the lamp, such as weighing bottles, extraction apparatus, volumetric ware, etc., causes the dealer the most trouble and inconvenience, mainly on account of the lack of skilled glass blowers. The workers naturally demand high wages under the

circumstances; consequently, most of these articles are much higher in price than formerly, and at a premium in some cases, which is due in a measure doubtless to the large educational demands. The workers do not readily conform to the usual conditions of labor, etc.; however, the situation is improving, but it is obvious that when hostilities cease the importation of the bulk of goods under this classification will be resumed.

(2) At the outbreak of the war there was a concern in this country making chemical porcelain, whose products were not at all satisfactory. They have wonderfully improved the line, however, until it is now practically equal to the best imported. Two or three other potteries have taken up the line, so that the market is now fairly well taken care of. Before these manufacturers got well under way, importations from Japan and Denmark were started, but their trade now appears to be confined chiefly to the educational institutions, on account of the lower duty-free prices.

(3) The majority of the generally-used articles under this classification were made in this country to advantage prior to the war, and there has been no changes of special note. A fair percentage of the miscellaneous assortment of articles that are not widely used were imported from Germany, so that in many cases they have been dispensed with now, as the demands do not warrant undertaking their manufacture in this country.

(4) A satisfactory grade of qualitative paper has been made in this country for many years. The quantitative papers were formerly imported exclusively from Germany and Sweden. Irregular shipments from Sweden are received, that by no means are sufficient to meet the demands, and the prices are considerably advanced, due to conditions in Sweden and high freights, etc. Consequently, the English papers, which are proving quite equal to the formerly used standards, are becoming widely used and increasingly popular. No one in this country appears to have taken up the manufacture of quantitative papers. These are all hand made, and as hand work is by no means an American specialty, it seems that we shall continue to use the foreign brands.

(5) For the last twenty years the American-made balances have increased in popularity, so that when the war started, imports consisted mainly of low-priced models entered duty free for edu-

cational institutions. As the number of skilled workers is limited and the demands greater than usual, all manufacturers are extremely busy.

(6) With exception of microscopes, of which there are several concerns here making excellent instruments, practically all articles under this classification were imported, and as the demands are small from a manufacturing point of view, the line with exception of a few very necessary articles, the manufacture of which has been undertaken in this country, is not available.

L. E. SAUNDERS (*Communicated*): In reading over the papers presented at this session and the discussion which followed them, I am more inclined than ever to insist that it is a condition, not a theory, that we are facing. We are obliged to judge of materials which we can purchase for electrochemical work, not on a strictly comparative basis, but on the basis of whether or not we can use them at all. If we approach trials of American-made materials in the spirit of fairness, I am firmly of the opinion that we will all be surprised at how many good things we shall find. If we are starting out, however, for the purpose of finding fault, faults will undoubtedly be seen. No European product, even, has ever come to my attention which is perfect.

I regret to note that comparatively little reference has been made to Mr. Schramm's most excellent digest of present conditions. This work is authoritative and worthy of our very best attention whenever we are taking up a trial of any of the articles mentioned; perhaps it is so very good that no one had quite nerve enough to criticise it.

A paper presented at the Thirtieth General Meeting of the American Electrochemical Society, held in New York City, September 28, 1916, Mr. L. E. Saunders in the Chair.

THE ELECTRODEPOSITION OF NICKEL.

By L. D. Hammond.

The voluminous literature on the electro-deposition of nickel abounds in contradictory statements concerning the conditions necessary for the electric current to deposit nickel from a given electrolyte. It also records a multiplicity of electrolytes which have been proposed, and testifies to the fact that the commercial application of the electro-deposition of nickel, commonly spoken of as "nickel plating," is not based upon scientific facts, but is an art practiced largely by those not thoroughly familiar with the fundamental principles of chemistry and electricity. Consequently, nickel plating, although it has been practiced for about fifty years, is still based upon "cut and try" methods.

These discrepancies have been mentioned by other writers[1] and a few examples will be cited. Langbein[2] states that the nickeling of cooking utensils is to be discouraged on account of the solubility of nickel in hot fats, vinegar, beer, mustard, tea, etc., while Bouant[3] states that nickel-plated utensils may be used in the kitchen as nickel salts do not harm the animal organism. Again, Langbein[4] states that "an alkaline reaction of nickel baths is absolutely detrimental," while Bennett[5] gives experimental data to show that a good deposit cannot be made from an acid electrolyte. However, many laboratory experiments and commercial practice testify that excellent deposits are obtained from electrolytes slightly acid in reaction.

A. Brochet[6] is sponsor for the statement that an electrolyte neutral in reaction is a necessary condition to secure a good

[1] Watts, Trans. Amer. Electrochem. Soc., 23, 123-147 (1913); Kalmus, Harper and Savelle, J. Ind. and Eng. Chem., 7, 380 (1915).

[2] Electro-deposition of Metals, p. 246.

[3] La Galvanoplastie, p. 186.

[4] Electro-deposition of Metals, p. 319.

[5] Trans. Amer. Electrochem. Soc., 25, 335-345 (1914).

[6] Metal Industry, 6, 314 (1908).

deposit of nickel, while Johnson[7] states that "nickel must be deposited from an alkaline, neutral or very slightly acid electrolyte." However, commercial practice in plating shows the necessity for maintaining the bath slightly acid. This condition is usually accomplished by the addition of boric acid, and, although its use for this purpose is very general, the function of boric acid in the electrolyte has never been explained.[8] This point will be discussed in detail later.

Again, Bennett[9] states that those electrolytes to which ammonium hydroxide was added "always gave a more adherent and better deposit" while the *Brass World*[10] in an article entitled "The Effect of Ammonium Hydroxide on Nickel Plating Solutions" finds that its presence is detrimental to a good deposit. Also the same journal,[11] as well as Hogaboom,[12] finds that copper salts in the electrolyte have a bad effect upon the nickel deposit, while Brown[13] states that copper in the anode is beneficial in that it increases anode corrosion. Bancroft[14] condemns the presence of iron in the plating bath to which presence he attributes the rusting of nickel plated articles, while the *Brass World*[15] says "at one time the presence of iron in the nickel deposit was looked upon as a very serious matter, but lately it not only has been looked upon less gravely, but in many instances is actually considered beneficial, particularly for certain kinds of work. Iron hardens the nickel when it is present in the deposit, and also produces a whiter color. To be sure, nickel containing a small quantity of iron tarnishes more readily, but even so it does not rust, but is subject only to the tarnish, which is not a serious matter on many classes of work."

Many of the earlier electrolytes proposed for nickel plating contained five or six different substances dissolved in water, but Watts[16] has stated that baths of simpler composition are to be preferred, and experiments recorded in this paper lead to the same conclusion. However, all of the unnecessarily complex

[7] Trans. Amer. Electrochem. Soc., **3**, 255 (1903).
[8] Langbein, Electro-deposition of Metals (1909), p. 249, and Trans. Amer. Electrochem. Soc., **27**, 118 (1915).
[9] Trans. Amer. Electrochem. Soc., **25**, 341 (1914).
[10] Brass World, **7**, 137 (1911).
[11] Brass World, **7**, 45 (1911).
[12] Trans. Amer. Electrochem. Soc., **23**, 269 (1913).
[13] Trans. Amer. Electrochem. Soc., **4**, 83 (1903).
[14] Trans. Amer. Electrochem. Soc., **9**, 218 (1906).
[15] Brass World, **7**, 154 (1911).
[16] Trans. Amer. Electrochem. Soc., **23**, 118 (1913).

baths have not been proposed in the past, as quite recently Mathers[17] has proposed one of this type, which will be discussed in detail later. Although several baths containing nothing but a nickel salt dissolved in water have been proposed,[18] Yates,[19] Powell,[20] and the *Brass World*[21] maintain that single salts cannot be used in plating. Brochet[22] states that, in order to secure a good deposit, a mixture of nickel sulphate and the chloride to which must be added an alkali salt is required, but it will be shown later that a good deposit can be obtained from nickel sulphate dissolved in water acidified with a small amount of hydrochloric acid. This solution contains all the factors necessary for a good deposit, so far as the electrolyte is concerned. Watts[23] has called attention to and criticized the statement of Sackur[24] that "good nickeling depends only on the choice of the right E. M. F., not upon the composition of the bath."

It has long been known that nickel anodes do not corrode satisfactorily and several methods have been proposed to overcome this difficulty. Brown[25] has measured the efficiency of anode corrosion in nickel-ammonium sulphate solution using anodes of electrolytic, rolled, and cast nickel. Cast anodes gave the highest efficiency, due to the impurities present, while the pure rolled anodes showed a very low efficiency. So commercial practice has sanctioned the addition of iron, carbon, and tin up to eight percent to overcome this so-called passivity of the nickel anode. Brown[26] approves of such practice while Bancroft[27] ascribes the rusting of nickel-plated objects to the presence of iron in the anode, which dissolves and deposits with the nickel, thus causing rusting. To avoid the rusting of nickel-plated objects, he proposes the use of pure nickel anodes and to induce good anode corrosion by the addition of ammonium chloride or nickel chloride to the electrolyte. Sodium chloride and magnesium chloride have also been proposed and used.

[17] Trans. Amer. Electrochem. Soc., 29, Apr., 1916.
[18] Watts, Trans. Amer. Electrochem. Soc., 23, 124-125 (1913).
[19] Trans. Amer. Electrochem. Soc., 23, 118 (1913).
[20] U. S. Patent, 229274, June 29, 1880.
[21] Brass World, 3, 129 (1907).
[22] Manual Pratique de Galvanoplastie (1908), p. 229.
[23] Trans. Amer. Electrochem. Soc., 23, 119 (1913).
[24] Elektrometallurgie, Peters, 4, 155.
[25] Trans. Amer. Electrochem. Soc., 4, 87 (1903).
[26] Trans. Amer. Electrochem. Soc., 4, 86 (1903).
[27] Trans. Amer. Electrochem. Soc., 9, 218 (1906).

Although Adams[28] states that "the art (of nickel plating) is today carried on substantially as it was in 1869-70, with the same solutions, the same anodes and the same details of shop manipulation," and although Foster[29] says that the trend of all improvement in nickel plating has been along mechanical lines, there has been a noticeable tendency to break away from the commonly used electrolyte, which consists chiefly of nickel ammonium sulphate. This has resulted from the introduction of the so-called "high power" or "rapid" plating solutions which, on account of their greater concentration of nickel salt, secured by the substitution of nickel sulphate for the less soluble nickel ammonium sulphate, permit a higher current density to be employed. These "high power" salts generally contain boric acid together with a chloride to insure anode corrosion. The most notable advance along this line has been the proposal of Watts[30] to use a concentrated solution of nickel sulphate to which is added nickel chloride and boric acid and to heat the bath to 70°. In this electrolyte, plating has been done at the current density of thirty-three amperes per square decimeter.

In view of these conflicting statements concerning the conditions best suited to the electro-deposition of nickel, the temptation was very great, both to inquire into them and to investigate some of the "rule of thumb" methods which have grown up with the plating industry. This paper reports the results of experiments made upon the corrosion of electrolytic nickel anodes, annealed electrolytic nickel anodes, and cast nickel anodes in various electrolytes; upon the conditions necessary for the direct deposition of nickel on zinc; and upon the use of boric acid in the electrolytes with the view of explaining its function.

I. ANODE CORROSION.

One of the important factors in the successful operation of a plating bath is the manner in which the anode corrodes. Under ideal conditions, nickel would dissolve at the anode at the same rate at which it is deposited at the cathode, and the composition of the bath would not be changed. If the rate of the solution at

[28] Trans. Amer. Electrochem. Soc., 9, 215 (1906).
[29] Metal Industry, 6, 8 (1908).
[30] Trans. Amer. Electrochem. Soc., 29, 395 (1916).

the anode is smaller than the rate of deposition at the cathode, the composition of the electrolyte will change, as its nickel content will decrease and the acid content increase. On the other hand, if the anode dissolves faster than the rate of deposition at the cathode, the nickel concentration of the electrolyte will increase and it will become alkaline in reaction. It has long been known that, when anodes of pure nickel are used, they soon fail to corrode properly and behave as the noble metals. This so-called passivity of the anode is remedied by substituting cast nickel anodes for the purer metals. An analysis of commercial anodes by Calhane and Gammage[31] showed about 7.5 percent of iron, and the metal deposited from these anodes contained from 0.07 to 0.75 percent of iron. The *Brass World*[32] states that impurities consisting of iron, tin and carbon "are introduced intentionally to render the anode 'soft,' *i. e.,* so that it will dissolve easily in the solution during plating." Although solution of anode is promoted by such practice, serious troubles result. The presence of the iron, tin, and carbon doubtless causes the anode to corrode on open circuit due to voltaic action. The more serious trouble, however, results from the fact that some iron is deposited along with the nickel, and the nickel plated object is coated, eventually, with rust.

Since the only kind of anodes obtainable are those containing iron, carbon, and tin, it was considered worth while to study the corrosion of electrolytic nickel in various electrolytes. Because the only electrolytic nickel available consists of rather thin sheets, some anodes were prepared by melting the electrolytic nickel and casting into bars $20 \times 4 \times 0.8$ cm. A second anode was prepared by taking a piece of the electrolytic nickel $17 \times 4.5 \times 0.3$ cm. and annealing it. The third was simply a piece of the electrolytic nickel $20 \times 4.5 \times 0.2$ cm. These anodes will be referred to as the cast, annealed, and electrolytic anodes respectively.

Brown [33] has pointed out the relation existing between the current efficiency of anode corrosion and the anode discharge potential in an electrolyte of nickel-ammonium sulphate, and it was deemed worth while to study anode corrosion in more modern electrolytes. The method of anode discharge potentials was not

[31] J. Amer. Chem. Soc., 29, 1268 (1907).
[32] Brass World, 7, 154 (1911).
[33] Trans. Amer. Electrochem. Soc., 4, 94 (1903).

employed, but advantage was taken of the fact, pointed out by Brown[33] that "a study of total polarization pressure, while not being as definite in the indications as a study of the individual electromotive force at the electrodes, will serve as a means for determining whether the cell is operating properly. When the polarization goes much above 0.75 volt, the assumption is justified that the anode is not corroding properly, and, on the other hand, if the polarization is below 0.7 volt, the efficiency at the anode is as high as can be obtained." Three different kinds of anodes were selected for this study as stated above. All of these anodes were prepared for the electrolyte by being scrubbed with powdered pumice, rinsed in cold water, subjected to the action of the electric cleaner for about ten seconds, rinsed in hot water and finally in cold. In all measurements the cathodes employed were of copper cleaned by being buffed, placed in the electric cleaner for about ten seconds and rinsed, first in hot, and then in cold water. The electrodes were then placed in the given electrolyte and the total polarization pressure at various current densities was read. In all cases the measurements were made at room temperature. All current densities are reported in amperes per square decimeter.

TABLE I.

Electrolyte: 120 gm. $NiSO_4.6H_2O$ per liter.

Amp.	Current Density			E. M. F. Volts			Polarization Volts		
	Cast.	Elec.	Anneal.	Cast.	Elec.	Anneal.	Cast.	Elec.	Anneal.
0.05	0.20	0.228	0.237	2.20	2.60	1.20	0.40	2.00	0.40
0.10	0.40	0.45	0.47	3.00	3.20	1.75	0.40	2.00	0.40
0.25	1.00	1.14	1.18	4.40	4.65	4.30	0.45	2.00	0.90
0.50	2.00	2.28	2.36	7.50	7.50	7.50	0.50	2.00	1.20
1.00	4.00	4.56	4.72	11.25	12.50	12.50	0.50	2.00	1.70
2.00	8.00	9.12	9.44	18.50	19.50	21.00	0.60	2.00	2.00
3.00	12.00	13.68	14.16	22.25	22.40	....	0.60	2.00	....
4.00	16.00	18.24	18.88	26.25	27.00	28.00	0.60	2.00	2.00

Table I.—At 12 amp. per sq. dm. the temperature had risen to 42° while at 16 it was 65°. The cathodes began to gas freely at a current density of 1 amp. The cast anode evolved gas at 8 amp. per sq. dm., while the first evolution of gas at the other two was noted at about 5 amp. All these cathodes gassed freely at the same rate. The electrolytic and annealed anodes evolved gas

freely, although not so rapidly as the cathodes, while the cast anode gassed at about half the rate of the other anodes. The electrolyte in which the cast anode was immersed became turbid and alkaline in reaction, while the others remained clear but became acid in reaction. The cast anode was slightly brownish black while the other two were metallic in appearance. All anodes showed signs of pitting. The cathodes were black at first, but at the higher current densities became covered with a green salt.

The data in Table I show that in an electrolyte containing only nickel sulphate dissolved in water, the cast anode corrodes satisfactorily, although it is less efficient at the higher current densities. The electrolytic anode corrodes very poorly from the start, while the effect of annealing is shown only at the lower densities. As the current density is increased the corrosion decreases, until finally this anode behaves as the unannealed one.

TABLE II.

Electrolyte: $NiSO_4.6H_2O$ 120 gm. and H_3BO_3 30 gm. per liter.

Amp.	Current Density			E. M. F. Volts			Polarization Volts		
	Cast.	Elec.	Anneal.	Cast.	Elec.	Anneal.	Cast.	Elec.	Anneal.
0.05	0.20	0.228	0.237	1.50	2.20	1.40	0.3	1.20	0.3
0.10	0.40	0.45	0.47	1.80	3.25	1.70	0.3	1.80	0.3
0.25	1.00	1.14	1.18	3.25	4.82	3.20	0.3	1.80	0.3
0.50	2.00	2.28	2.36	6.25	7.50	6.00	0.3	1.80	0.3
1.00	4.00	4.56	4.72	10.00	10.70	11.50	0.3	1.80	0.3
2.00	8.00	9.12	9.44	14.75	14.50	....	0.3	1.50	..
3.00	12.00	13.68	14.16	21.00	19.50	....	0.3	1.40	..
4.00	16.00	18.24	18.88	23.60	22.50	....	0.3	1.30	..

Table II.—At about 8 amp. per sq. dm. the electrolytic and annealed anodes were gassing freely, while the cathodes were evolving gas but feebly at twice that current strength. At the cast anode a few bubbles were occasionally seen. The electrolytic and annealed anodes were bright, and the cast anode was black around the pitted portions, although otherwise bright. The electrolytes were clear, with the exception of that of the cast anode, which was turbid.

The data in Table II show that in the boric acid solution the corrosion of the cast and annealed anodes is very satisfactory. At the lowest current densities the electrolytic anode corrodes

slightly better than in the previous electrolyte. As the current strength is increased this anode becomes more passive, but at the highest current densities the corrosion is the same as at the lowest current densities.

TABLE III.

Electrolyte:

$NiSO_4.6H_2O$ 120 gm.; H_3BO_3 30 gm.; $NiCl_2.6H_2O$ 5 gm. per liter.

Amp.	Current Density			E. M. F. Volts			Polarization Volts		
	Cast.	Elec.	Anneal.	Cast.	Elec.	Anneal.	Cast.	Elec.	Anneal.
0.05	0.20	0.228	0.237	1.10	2.25	1.00	0.20	1.20	0.20
0.10	0.40	0.45	0.47	1.65	3.08	1.35	0.20	1.60	0.20
0.25	1.00	1.14	1.18	2.70	4.60	2.45	0.20	1.70	0.20
0.50	2.00	2.28	2.36	5.70	7.00	4.25	0.20	1.50	0.15
1.00	4.00	4.56	4.72	14.00	12.00	8.00	0.40	1.50	0.10
2.00	8.00	9.12	9.44	19.75	20.50	15.00	0.50	1.50	0.20
3.00	...	13.68	14.16	....	28.50	22.50	...	1.80	0.30

Table III.—At a current density of 12 amp. the temperature rose to 30°. At 5 amp. the cathodes began to evolve gas and as the current density became greater the gas evolution correspondingly increased. At about 2 amp. the anodes began to liberate gas.

The data in Table III show that nickel chloride to the extent of 5 gm. per liter causes marked corrosion of both the cast and annealed anodes as was to be expected, and, although at the lowest current densities the corrosion of the electrolytic anode was improved, its behavior was still unsatisfactory.

TABLE IV.

Electrolyte:

$NiSO_4.6H_2O$ 120 gm.; H_3BO_3 30 gm.; $NiCl_2.6H_2O$ 10 gm. per liter.

Amp.	Current Density			E. M. F. Volts			Polarization Volts		
	Cast.	Elec.	Anneal.	Cast.	Elec.	Anneal.	Cast.	Elec.	Anneal.
0.05	0.20	0.228	0.237	1.05	2.08	1.30	0.20	1.20	0.2
0.10	0.40	0.45	0.47	1.60	3.15	1.55	0.20	1.20	0.2
0.25	1.00	1.14	1.18	3.00	4.80	2.90	0.20	1.20	0.2
0.50	2.00	2.28	2.36	5.40	7.50	5.10	0.20	1.20	0.2
1.00	4.00	4.56	4.72	10.75	12.40	9.00	0.45	1.20	0.2
2.00	8.00	9.12	9.44	20.25	20.00	17.10	0.50	1.20	0.2
3.00	12.00	13.68	14.16	27.50	29.00	25.00	0.50	1.40	0.3

Table IV.—At 12 amp. per sq. dm. the temperature rose to 28°. Table IV shows that the addition of nickel chloride to the concentration of 10 gm. per liter materially increases the corrosion of the electrolytic anode, although it still does not corrode satisfactorily.

TABLE V.

Electrolyte:

$NiSO_4.6H_2O$ 120 gm.; H_3BO_3 30 gm.; $NiCl_2.6H_2O$ 15 gm. per liter.

Amp.	Current Density			E. M. F. Volts			Polarization Volts		
	Cast.	Elec.	Anneal.	Cast.	Elec.	Anneal.	Cast.	Elec.	Anneal.
0.05	0.20	0.228	0.237	1.05	1.15	1.20	0.20	0.2	0.2
0.10	0.40	0.45	0.47	1.40	1.60	1.40	0.50	0.3	0.2
0.25	1.00	1.14	1.18	2.64	3.50	2.80	0.50	0.4	0.2
0.50	2.00	2.28	2.36	4.75	6.50	4.50	0.45	0.4	0.2
1.00	4.00	4.56	4.72	8.75	11.00	7.75	0.45	0.5	0.2
2.00	8.00	9.12	9.44	15.00	17.50	16.00	0.45	0.6	0.25
3.00	12.00	13.68	14.16	20.50	25.00	23.00	0.50	0.7	0.30
4.00	16.00	18.24	18.88	24.75	....	....	0.50	..	...

Table V.—At 12 amp. per sq. dm. the temperature rose to 36°, and at 16 amp. it was 40°. At 5 amp. there was a slight gassing at both cathodes and at the electrolytic and annealed anodes. The electrolyte of the cast anode was turbid and alkaline, and, upon standing, nickelous hydroxide precipitated. The other electrolytes were clear and acid in reaction. The anodes were bright and slightly pitted.

The data of Table V show that with a concentration of nickel chloride at 15 gm. per liter the electrolytic anode corrodes very well.

TABLE VI.

$NiSO_4.6H_2O$ 120 gm.; H_3BO_3 30 gm.; $NiCl_2.6H_2O$ 30 gm. per liter.

Amp.	Current Density			E. M. F. Volts			Polarization Volts		
	Cast.	Elec.	Anneal.	Cast.	Elec.	Anneal.	Cast.	Elec.	Anneal.
0.05	0.20	0.228	0.237	0.95	1.00	1.05	0.2	0.2	0.15
0.10	0.40	0.45	0.47	1.40	1.45	1.30	0.2	0.2	0.15
0.25	1.00	1.14	1.18	2.65	3.00	2.20	0.2	0.4	0.15
0.50	2.00	2.28	2.36	4.45	5.00	4.25	0.2	0.4	0.10
1.00	4.00	4.56	4.72	8.50	9.50	7.00	0.2	0.4	0.10
2.00	...	9.12	9.44	...	16.50	13.00	..	0.4	0.10
3.00	...	13.68	14.16	...	23.00	19.00	..	0.5	0.15
4.00	...	18.24	18.88	...	28.50	23.25	..	0.7	0.20

Table VI.—At 5 amp. per sq. dm. the temperature rose to 29°, while at 16 amp. it was 35°. Gas was evolved at all electrodes except the annealed anode. When removed from the electrolyte the anodes were all bright. As is to be expected, all anodes corrode well. Both the cast and annealed show better corrosion than in the previous electrolytes, but doubling the concentration of the nickel chloride does not materially change the corrosion of the electrolytic anode.

In Table VII are given the results of measurements of total polarization pressures, using an electrolytic nickel anode and copper cathode in an electrolyte of 40 gm. of nickel sulphate per liter, to which progressive additions of nickel chloride were made.

TABLE VII.

Grams per Liter of $NiCl_2.6H_2O$	Amp.	Current Density	E. M. F. Volts	Polarization Volts
0	0.1	0.20	2.80	2.00
1	0.1	0.20	2.80	1.70
2	0.1	0.20	2.75	1.60
4	0.1	0.20	2.68	1.30
6	0.1	0.20	1.78	0.60

From Table VII it will be seen that 6 gm. per liter of nickel chloride are required as the minimum amount necessary to produce fair corrosion, although 15 gm. per liter (Table V) are necessary to secure the best results.

In Table VIII are given the results of current efficiency measurements with the anodes and electrolytes used in making the total polarization pressure measurements. Copper cathodes were used in all cases and their efficiencies were also measured.

TABLE VIII.

Electrolyte, gm. per liter	C. D.	Current Efficiency					
		Cast Anode		Elec. Anode		Annealed Anode	
		Corr.	Dep.	Corr.	Dep.	Corr.	Dep.
$NiSO_4.6H_2O$ 120....	0.5	107.4	58.32	38.50	42.53	74.30	42.94
$NiSO_4.6H_2O$ 120.... H_3BO_3 30.....	0.5	97.57	96.31	45.81	47.23	102.80	97.47
$NiSO_4.6H_2O$ 120.... H_3BO_3 30..... $NiCl_2.6H_2O$ 10.....	0.5	96.25	94.98	98.52	97.45	109.1	98.16

Table VIII.—These figures confirm in a quantitative manner the indications of anode corrosion shown by the total polarization pressures. This study of anode corrosion shows that, although cast anodes corrode fairly well in the simple sulphate electrolytes to which boric acid has been added, the best practice is to use the purest electrolytic nickel and to use nickel chloride to secure good corrosion. Nickel chloride is to be preferred to other chlorides, as its addition does not decrease the concentration of nickel in the electrolyte. It has been shown that 6 gm. per liter of nickel chloride will produce good anode corrosion, and that the best results are secured by increasing the nickel chloride to 15 gm. per liter.

II. THE DIRECT NICKELING OF ZINC.

Attention is being attracted to the direct deposition of nickel on zinc owing to the increased use of zinc to cover tables, kitchen cabinets, etc., and to its use in die castings, which are largely zinc. Langbein[34] states that "sheet zinc directly nickeled does not show the warm, full tone of sheets previously coppered or brassed. The nickel deposit on brassed sheets shows a decidedly whiter tone than on copper sheets, and brassing would deserve the preference if this process did not require extraordinarily great care in the proper treatment of the bath, the nickel deposit readily peeling off." Experiment has shown that all of the baths proposed for the direct nickeling of zinc give a deposit of yellowish nickel, but that this can be remedied by the addition of acid to the bath.

The direct nickeling of zinc presents difficulties not encountered in the deposition of nickel upon copper or brass, due to the fact that zinc is more electro-positive than nickel, so that, when the zinc is placed in the electrolyte, a non-adherent deposit of black nickel immediately appears, which causes the metal, afterward deposited on the zinc by the current, to peel. In order to avoid the trouble caused by this deposition by immersion two methods are in use at present. One is to coat the zinc first with a more negative metal or alloy, such as copper or brass, which can be done in an electrolyte containing potassium cyanide, since the copper or brass becomes more positive in such a solution, and the difference between the single potentials of zinc and copper is so

[34] Electro-deposition of Metals, p. 298.

small that deposition by immersion does not occur. However, this method involves a second operation which, from a commercial viewpoint, makes the process more expensive. The second method is to subject the article to be plated for about thirty seconds to an initial current density much higher than that regularly employed. This is called "striking."

In looking over the electrolytes that have been proposed[35] for the direct nickeling of zinc, it is seen that they are all low in nickel content, which permits only a small current density to be employed, and that other substances have been added, such as magnesium sulphate, potassium or sodium citrate, phosphates, bisulphites, etc., which are for the purpose of making the zinc less positive to the electrolyte. It is the object of this part of the paper to report the results of study made first, to find out the purpose of these added substances; second, to see if they make the zinc less positive; and, third, to see if nickel cannot be directly deposited more rapidly than from the baths already proposed.

To see if there was any change in the relative potentials of the zinc and nickel it was decided to measure their potentials in the various baths proposed for the direct nickeling of zinc. The Poggendorf compensation method was employed together with the normal calomel electrode, the potential of which was taken as —0.56 volt. The measurements were all made at room temperature.

TABLE IX.

Electrolyte	Metal	Single Potential
Nickel sulphate ..... 40 gm. Sodium citrate ..... 35 gm. Water ..... 1000 cc.	Ni	0.205
Same electrolyte	Zn	0.55
Nickel ammonium sulphate ..... 56 gm. Magnesium sulphate ..... 26 gm. Water ..... 1000 cc.	Ni	0.20
Same electrolyte	Zn	0.498
Ammonium chloride ..... 37.5 gm. Nickel chloride ..... 37.5 gm. Water ..... 1000 cc.	Ni	0.28
Same electrolyte	Zn	0.51

[35] Watts, Trans. Amer. Electrochem. Soc., 23, 149 (1913).

Table IX shows that, in the baths proposed for the direct nickeling of zinc, the single potentials of both nickel and zinc have practically the same values as in normal solutions of their salts. The zinc is not less positive in these baths and should precipitate nickel by immersion. In all these baths it was found that such was the case. It will be shown later that sodium citrate slows down the rate with which the deposition by immersion takes place, and it is to this effect that its beneficial action is due.

Several of the baths which have been proposed for the direct nickeling of zinc were prepared and tested. Of those tried only one proved satisfactory. This was the one proposed by Pfanhauser,[36] consisting of 40 gm. of nickel sulphate and 35 gm. of sodium citrate per liter. At a current density of 0.5 amp. and E. M. F. of 2.7 volts the total polarization pressure was 1.8 volts, indicating very poor anode corrosion, which was to be expected from the absence of any chloride. The deposit, however, was adherent and of a yellowish tint. Similar baths proposed by Langbein[37] and by Proctor[38] contain potassium citrate and ammonium chloride and should give good deposits. All these baths are low in nickel content and so can be operated only at small current densities. Since the rate of deposition by immersion increases with the increase of the concentration of nickel salt, it is not surprising that these dilute solutions were used. However, more concentrated solutions have been successfully employed, as will be shown later.

Two other baths proposed by Langbein[37] were prepared and tried, but they did not yield good deposits. One contained 56 gm. of nickel-ammonium sulphate and 26 gm. of magnesium sulphate per liter, while the other contained 37 gm. each of nickel chloride and ammonium chloride per liter. The bath proposed by Proctor in the *Metal Industry*[39] gives satisfactory deposits, but, as will be shown later, it contains unnecessary components and in its stead a simpler bath is proposed.

It was noted, in the baths proposed for the direct nickeling of zinc, that if a piece of zinc were immersed in the electrolyte, it would finally be coated by immersion; therefore, it was decided

[36] Elektroplattirung, W. Pfanhauser (1900).
[37] Electro-deposition of Metals, p. 319 (1909).
[38] Metal Industry, **9**, 353 (1911).
[39] Metal Industry, **13**, 274 (1915).

to determine how the rate of deposition by immersion was affected by changes of temperature. For this purpose a bath proposed by Pfanhauser[40] was chosen which had the following composition:

Nickel sulphate	40 gm
Sodium citrate	35 gm.
Water	1000 cc.

Strips of zinc were polished, cleaned in the electric cleaner, immersed in the electrolyte, and the temperature, time and the character of the deposit noted.

TABLE X.

Temp.	Time	Deposit
0°	15 min.	None.
0°	30 min.	None.
0°	45 min.	Slight coloration.
18.5°	15 min.	Slight coloration, hardly as much as above.
18.5°	30 min.	Decided yellow color.
18.5°	45 min.	Black brown.
45°	10 sec.	None.
45°	30 sec.	Perceptible color of yellow.
45°	60 sec.	Decided yellow.
60°	10 sec.	Perceptible yellow.
60°	20 sec.	Yellow.
60°	30 sec.	Decided yellow.
75°	10 sec.	More than perceptible.
75°	20 sec.	Decided yellow.
75°	30 sec.	Brownish black.
90°	5 sec.	Decidedly perceptible.
90°	10 sec.	Yellow.
90°	15 sec.	Brown.
90°	20 sec.	Blue black.

The data of Table X show why hot solutions, which have been so advantageously employed in nickeling copper, for example, cannot be used in the direct deposition of nickel on zinc, since the rate of deposition by immersion increases with increase of temperature. Experience has also shown that this rate, even at ordinary temperature, is increased with the increase of concentration of nickel salt in the electrolyte. This fact explains why all the baths proposed for the direct nickeling of zinc are low in nickel.

In examining the conditions necessary for the direct deposition of nickel on zinc, the following data show the relation between the character of the deposit and the composition of the electrolyte and current density employed. Twenty different electrolytes were

[40] Elektroplattirung, W. Pfanhauser, 1900.

studied, in which the nickel sulphate varied in concentration from 40 gm. per liter to a saturated solution. Some of these were used without the addition of any other substance, while in other solutions nickel chloride was added. Still others contained varying amounts of nickel sulphate and nickel chloride acidified separately with various acids. The current density varied all the way from 0.2 amp. to 15 amp. per square decimeter. These experiments show that nickel can be deposited directly on zinc from an electrolyte of any concentration of nickel which is acid in reaction and contains nickel chloride to secure proper anode corrosion. It is only necessary to vary the current density employed, which must be increased as the concentration of nickel increases. It is not absolutely necessary to add sodium citrate or magnesium sulphate to the electrolyte, although the presence of the former is advantageous, as will be discussed later.

Langbein[41] states that the bath for the direct nickeling of zinc containing citrate must be kept strictly neutral, but experiment has shown this statement to be untrue. The bath proposed by Pfanhauser[42] consisting of nickel sulphate 40 gm. and sodium citrate 35 gm. per liter was prepared and a strip of zinc was plated at 0.27 amp., the current density recommended. The deposit was metallic and adherent, but of a dark yellow tint. The current density was increased to one ampere with no change in the character of the metal deposited. Boric acid to the extent of 30 gm. per liter was added, and at 1 amp. a fine deposit was obtained of much lighter shade than before. However, there was a total polarization pressure of 1.8 volts showing that the anode was not corroding properly. Upon adding nickel chloride to a concentration of 10 gm. per liter, the character of the deposit was not changed, but the total polarization value of 0.5 volt showed that the anode was corroding properly. Thus by adding acid to Pfanhauser's bath, a whiter nickel is produced, and the addition of nickel chloride permits the bath to be operated at a current density four times that of the original bath and with a smaller consumption of power.

Table XI shows the effect of the addition of sodium citrate to the baths for the direct nickeling of zinc.

[41] Langbein, Electro-deposition of Metals, p. 151.
[42] Electroplattirung, W. Pfanhauser (1900).

TABLE XI.

Electrolyte, gm. per liter	Amp.	C. D.	E. M. F. Volts	Polarization Volts	Deposit
$NiSO_4.6H_2O$ 40 $NiCl_2.6H_2O$ 10 H_3BO_3 30	0.10	1.00	2.60	0.6	Yellow, adherent.
$NiSO_4.6H_2O$ 55 $NiCl_2.6H_2O$ 10 H_3BO_3 30	0.10	1.00	2.50	0.6	Yellow, adherent.
$NiSO_4.6H_2O$ 120 $NiCl_2.6H_2O$ 10 H_3BO_3 30	0.10	1.00	2.20	0.6	White streaks, polished yellow.
	0.20	2.00	3.20	0.6	Not so streaked.
	0.30	3.00	4.58	0.6	Matte, polished well. This is as good a deposit as the modified Pfanhauser bath.
	0.40	4.00	5.60	0.6	Unsatisfactory.
$NiSO_4.6H_2O$ 120 $NiCl_3.6H_2O$ 10 H_3BO_3 30 $Na_3C_6H_5O_7$ 35	0.10	1.00	1.80	0.6	Black.
	0.20	2.00	3.20	0.6	Good.
	0.30	3.00	4.10	0.6	Matte, polished well.
$NiSO_4.6H_2O$ 120 $NiCl_2.6H_2O$ 10 H_3BO_3 30 $Na_3C_6H_5O_7$ 70	0.10	1.00	2.80	0.6	Good.
	0.20	2.00	3.50	0.6	Matte, fine.
$NiSO_4.6H_2O$ 240 $NiCl_2.6H_2O$ 10 H_3BO_3 30	0.10	1.00	2.60	0.8	Brown streaks.
	0.20	2.00	3.20	0.8	Brown streaks, but not so many.
	0.30	3.00	3.60	0.8	Brown streaks, but still less.
	0.40	4.00	4.00	0.8	Matte, few brown streaks.
	0.50	5.00	4.75	0.8	Matte, polished bright around edges, but dull in middle area.
	0.60	6.00	5.20	0.8	Matte, polished well.
$NiSO_4.6H_2O$ 240 $NiCl_2.6H_2O$ 10 H_3BO_3 30 $Na_3C_6H_5O_7$ 70	0.10	1.00	2.70	0.6	Slightly streaked.
	0.20	2.00	3.25	0.6	Matte, except few areas.
	0.30	3.00	3.70	0.6	Matte, fine.
$NiSO_4.6H_2O$ 240 $NiCl_2.6H_2O$ 10 H_3BO_3 30 $Na_3C_6H_5O_7$ 105	0.10	1.00	2.80	0.5	Brown lines.
	0.20	2.00	3.25	0.5	Matte, fine.
	0.30	3.00	3.85	0.5	Matte, fine.
$NiSO_4.6H_2O$ 240 $NiCl_2.6H_2O$ 10 H_3BO_3 30 $Na_3C_6H_5O_7$ 140	0.10	1.00	2.75	0.5	Small areas of irreg. dep.
	0.20	2.00	3.20	0.5	Good. Slight irreg. in center.
	0.30	3.00	3.72	0.5	Matte, fine.
$NiSO_4.6H_2O$ 240 $NiCl_2.6H_2O$ 10 H_3BO_3 30 $Na_3C_6H_5O_7$ 175	0.05	0.50	2.50	0.5	Bright, fine.
	0.10	1.00	2.75	0.5	Bright, fine.
	0.20	2.00	3.30	0.5	Slightly matte, fine.
	0.40	4.00	3.90	0.5	5 min. dep. curled on edges; 2 min. dep. fine.
	0.60	6.00	5.05	0.5	2 min. dep. burned on edges; 1 min. dep. fine.
	0.70	7.00	5.30	0.5	1 min. dep. fine.

Table XI brings out very clearly the effect of the sodium citrate on the bath for the direct deposition of nickel on zinc. In the first place, it is demonstrated that sodium citrate is not necessary for a good deposit of nickel directly on zinc. With a small concentration of nickel good deposits are made at a current density of 1 ampere, which is four times the rate employed in Pfanhauser's bath. As the concentration of nickel sulphate was increased to 120 gm. per liter, the current density required to secure a good deposit was 3 amp. per square decimeter. This deposit was excellent, and was as good as the one obtained by adding nickel chloride and boric acid to Pfanhauser's bath. The addition of sodium citrate to the extent of 35 gm. per liter gave a good deposit at a current density of 2 amperes, while only 1 amp. was required to secure a good deposit when 70 gm. per liter of sodium citrate were used. When the concentration of nickel sulphate was increased to 240 gm. per liter, the minimum current density for a good deposit was 5 amp. The addition of 70 gm. of sodium citrate per liter lowered the minimum current density for a good deposit to 3 amp., and as the citrate was increased, the current density required for a good deposit decreased, until, upon the addition of 175 gm. per liter, a bright deposit was secured at the low current density of 0.5 ampere.

In Table XII the data show the effects of the separate additions of progressively increasing amounts of sodium succinate, sodium malate, and sodium potassium tartrate on the character of the nickel deposits made directly on zinc.

TABLE XII.

		Amp.	C. D.	E. M. F. Volts	Polarization Volts	Deposit
$NiSO_4.6H_2O$	240	0.10	1.00	1.70	0.5	Bright with some brown streaks.
$NiCl_2.6H_2O$	10	0.20	2.00	2.20	0.5	Bright, white.
H_3BO_3	30	0.30	3.00	3.20	0.5	Bright, white, edges slightly burned.
$KNaC_4H_4O_6.4H_2O$	35					
$NiSO_4.6H_2O$	240	0.10	1.00	1.90	0.5	Fine. Slight brown area at top of cathode.
$NiCl_2.6H_2O$	10	0.20	2.00	2.25	0.5	Brown areas, polished well.
H_3BO_3	30	0.30	3.00	3.60	0.5	Matte. Polished well.
$KNaC_4H_4O_6.4H_2O$	70	0.40	4.00	4.00	0.5	Matte. Edges slightly burned. Polished well.

TABLE XII (*Continued*).

		Amp.	C. D.	E. M. F. Volts	Polarization Volts	Deposit
$NiSO_4.6H_2O$	240	0.05	0.50	1.45	0.5	Bright, adherent.
$NiCl_2.6H_2O$	10	0.10	1.00	1.90	0.5	Matte. Polished well.
H_3BO_3	30	0.20	2.00	3.00	0.5	Burned, unsatisfactory.
$KNaC_4H_4O_6.4H_2O$	105	0.20	2.00	3.00	0.5	Burned, unsatisfactory.
$NiSO_4.6H_2O$	240	0.05	0.50	1.50	0.5	Bright. Small brown areas.
$NiCl_2.6H_2O$	10	0.10	1.00	2.50	0.5	Bright, adherent.
H_3BO_3	30	0.20	2.00	3.00	0.5	Bright. Edges rough.
$KNaC_4H_4O_6.4H_2O$	140	0.30	3.00	3.50	0.5	Rough, unsatisfactory.
		0.05	0.50	1.55	0.5	Yellow, brown streaks, polished well.
		0.10	1.00	2.70	0.5	Yellow, brown streaks, polished well.
$NiSO_4.6H_2O$	240					
$NiCl_2.6H_2O$	10	0.20	2.00	3.20	0.5	Slightly burned on edges, rough areas.
H_3BO_3	30					
$KNaC_4H_4O_6.4H_2O$	175	0.30	3.00	3.60	0.5	Slight burned on edges, rough areas.
		0.40	4.00	4.15	0.5	Burned, unsatisfactory.
		0.05	0.50	1.20	0.5	Brown streaks.
		0.10	1.00	1.50	0.5	Fine brown lines.
$NiSO_4.6H_2O$	240	0.20	2.00	2.10	0.5	Fine brown lines.
$NiCl_2.6H_2O$	10	0.30	3.00	2.55	0.5	Fine brown lines. so many.
H_3BO_3	30					
$Na_2C_4H_4O_4.6H_2O$	35	0.40	4.00	3.00	0.5	Better, but not satisfac-factory.
		0.05	0.50	1.20	0.5	Black.
$NiSO_4.6H_2O$	240	0.10	1.00	1.62	0.5	Brown lines.
$NiCl_2.6H_2O$	10	0.20	2.00	2.10	0.5	Brown lines, but not so many.
H_3BO_3	30	0.30	3.00	2.70	0.5	Fine brown lines.
$Na_2C_4H_4O_4.6H_2O$	70	0.40	4.00	2.88	0.5	Matte. Burned on edges.
		0.50	5.00	3.00	0.5	Matte. Burned on edges.
		0.05	0.50	1.10	0.5	Brown lines.
		0.10	1.00	1.45	0.5	Brown lines.
$NiSO_4.6H_2O$	240	0.20	2.00	1.90	0.5	Few brown lines. Polished well.
$NiCl_2.6H_2O$	10					
H_3BO_3	30	0.30	3.00	2.15	0.5	Matte. Polished well.
$2Na_2C_4H_4O_5.H_2O$	35	0.40	4.00	2.60	0.5	Matte. Polished well.
		0.50	5.00	3.20	0.5	Matte. Polished well.
$NiSO_4.6H_2O$	240	0.05	0.50	1.20	0.5	Brown lines. Non-adherent.
$NiCl_2.6H_2O$	10	0.10	1.00	1.45	0.5	Matte. Polished well.
H_3BO_3	30	0.20	2.00	1.95	0.5	Matte. Polished well.
$2Na_2C_4H_4O_5.H_2O$	70	0.30	3.00	2.50	0.5	Matte. Polished well.
$NiSO_4.6H_2O$	240	0.05	0.50	1.20	0.5	Non-adherent.
$NiCl_2.6H_2O$	10	0.10	1.00	1.52	0.5	Matte. Polished well.
H_3BO_3	30	0.20	2.00	2.10	0.5	Matte. Polished well.
$2Na_2C_4H_4O_5.H_2O$	105					

Table XII.—One hundred seventy-five grams per liter of potassium sodium tartrate can be added to a solution of 240 gm. per liter of nickel sulphate without producing a precipitate. The addition of 35 and of 70 gm. per liter of sodium succinate to a nickel sulphate solution of the same concentration produced a slight precipitate, which was removed. One hundred five grams per liter of sodium succinate produced such a copious precipitate as to render the bath unfit for use. The successive additions of sodium malate produced a slimy, green coating on the cathode. It has been shown that sodium citrate decreases the rate of deposition by immersion and the data in this table show that the addition of sodium potassium tartrate and sodium malate to the nickel bath has the same effect. Sodium potassium tartrate to the extent of 105 gm. per liter will permit nickel to be deposited directly on zinc at a current density of 0.5 ampere per sq. dm., while 175 gm. per liter of sodium citrate were required to produce the same result. On the other hand, the citrate bath can be successfully operated at a current density of 7 amp. per sq. dm., while 3 amp. per sq. dm. is the maximum current density for the tartrate bath. The addition of 70 gm. per liter of sodium malate produced a good deposit at a current density of 1 amp. per sq. dm. The cathode was always covered with a slimy green coating and it was impossible to obtain a good deposit at a current density lower than 1 amp. The addition of sodium succinate failed to produce a good deposit. It is of interest that the sodium or potassium salts of succinic acid do not produce a good deposit of nickel on zinc, while the same salts of malic acid (monohydroxysuccinic acid) and tartaric acid (dihydroxysuccinic acid) do produce good deposits. Furthermore, sodium citrate, which also produces a good deposit directly on zinc, is the sodium salt of hydroxytricarballylic acid. These experiments show that the production of a good deposit of nickel directly on zinc is related in some way to the presence of the hydroxyl group. This matter is reserved for further inquiry.

Thus it will be seen that, while either sodium potassium tartrate or sodium malate can be substituted for sodium citrate in baths used for the direct nickeling of zinc, sodium citrate is to be preferred on account of its greater solubility and on account of the fact that it permits the use of a wider range or current densities.

Proctor[43] proposes the following bath for the direct nickeling of zinc:

$NiSO_4.(NH_4)_2SO_4.6H_2O$	60	gm.
$NiSO_4.6H_2O$	15	"
NH_4Cl	15	"
$MgSO_4.H_2O$	30	"
H_3BO_3	7.5	"
H_2O	1000	cc.

Anodes of rolled sheet steel were advised, with an E. M. F. of 3.5 volts. Using electrolytic nickel anodes, a metallic, yellowish, adherent deposit was secured at a current density of 1 amp. and an E. M. F. of 1.35 volts. A bath was next prepared in which all ammonium salts were excluded, but the nickel, boric acid, and chloride contents were kept the same and the magnesium sulphate was retained. It had the following composition:

$NiSO_4.6H_2O$	55	gm.
$MgSO_4.H_2O$	30	"
H_3BO_3	7.5	"
$NiCl_2.6H_2O$	3.5	"
H_2O	1000	cc.

Using a current density of 1 amp. at 3.65 volts the deposit was uneven with dark and yellow areas. Upon the addition of boric acid sufficient to increase its concentration to 30 gm. per liter, and electrolyzing under the same conditions, a fine deposit of yellowish tint resulted. The following electrolyte was then prepared:

$NiSO_4.6H_2O$	55	gm.
$NiCl_2.6H_2O$	10	"
H_3BO_3	30	"
H_2O	1000	cc.

From this bath, a fine, adherent deposit of yellowish nickel was obtained under the same electrolyzing conditions just mentioned. This shows that the magnesium sulphate plays no part in determining the physical properties of the deposited metal. The fact, that in the absence of the ammonium salts an unsatisfactory deposit was obtained and that a good one resulted when the concentration of boric acid was increased, shows that a good deposit can be secured only in the presence of some substance which will

[43] Metal Industry, 13, 274 (1915).

dissolve basic salts that precipitate on the cathode and spoil the deposit. In the first case ammonium salts dissolved the basic nickel salt that tended to precipitate, while in the second case this result was accomplished by boric acid. Thus is demonstrated the reason why in those baths containing no acid, the much-used nickel ammonium sulphate and ammonium chloride have been preferred to nickel chloride and the more soluble nickel sulphate.

Owing to the more electro-positive nature of zinc, it is more difficult to deposit a good coating of nickel on this metal than on a more negative metal, such as copper, on account of the trouble caused by the deposition of nickel by immersion, which causes the electrolytic deposit to peel. It has therefore been thought necessary to add substances to the electrolyte to make the zinc less positive. Single potential measurements, however, show that the potential of the zinc has not been changed, and experiment has shown that these substances do not alter the character of the deposit. Zinc may be nickeled directly from the same bath used for copper or for brass, the only difference being in the current density which it is necessary to employ. Zinc requires a higher current density, especially at the beginning of the electrolysis, to coat the metal quickly with nickel so as to minimize deposition by immersion. The greater the concentration of nickel in the electrolyte, the greater must be the initial current density used. It has been found, however, that alkaline citrates, tartrates and malates reduce the initial current density necessary to be employed with concentrated nickel solutions.

An electrolyte of the following composition was prepared:

$NiSO_4.6H_2O$	120 gm.
$NiCl_2.6H_2O$	15 "
H_3BO_3	30 "
H_2O	1000 cc.

This bath may be used to give a deposit on zinc, copper, brass or iron. In order to deposit on copper, a current density varying from a few tenths of an ampere to three or four may be used, but to deposit on zinc, not less than 3 amp. can be employed, which will produce a coating of nickel on a piece of zinc in one-twelfth of the time required for Pfanhauser's bath.

While excellent results were obtained from this bath when flat pieces of zinc in the form of strips were used, it is possible that,

when zinc objects of irregular form are to be plated, black streaks may be formed on those parts of the object which may be subjected to a lower current density. In order to overcome this difficulty, the following new bath is proposed for the direct and rapid nickeling of zinc:

$NiSO_4.6H_2O$	240 gm.
$NiCl_2.6H_2O$	15 "
H_3BO_3	30 "
$2Na_3C_6H_5O_7 11H_2O$	175 "
H_2O	1000 cc.

This bath has been operated at current densities varying from 0.5 to 7 amperes per square decimeter and satisfactory deposits were secured. Pure electrolytic nickel anodes should be used.

In all the baths for the direct nickeling of zinc there is a lack of acid, except in those proposed within the last few years, which contain boric acid. However, this is such a weak acid that there is no appreciable action on the zinc even on open circuit. It has been shown, however, that nickel can be deposited directly on zinc from electrolytes strongly acid in reaction. Not only have fairly concentrated solutions of organic acids been used, but the strong mineral acids also. Table XIII shows the effect, on the character of the deposit, of progressive additions of 4N hydrochloric acid to an electrolyte of the following composition:

$NiSO_4.6H_2O$	160 gm.
$NiCl_2.6H_2O$	6 "
H_2O	1000 cc.

This experiment was carried out with 250 cubic centimeters of the above electrolyte, to which the indicated volumes of the acid were added.

TABLE XIII.

cc. 4NHCl added	Amp.	C. D.	E. M. F. Volts	Polar. Volts	Deposit
0	2.00	8.33	10.00	2.00	Green, non-adherent.
1	2.00	8.33	10.00	2.00	" " "
1	1.00	4.16	9.00	2.00	" " "
3	0.74	3.08	8.00	1.80	" " "
5	0.84	3.50	8.00	0.95	" " "
10	1.00	4.16	8.00	0.70	Metallic, buffed off.
5	1.80	7.50	8.00	0.70	Metallic, yellow, stood buffing.
5	2.20	9.16	6.00	0.60	Bright, yellowish, adherent.

Table XIII shows that with the successive additions of hydrochloric acid, the passivity of the electrolytic nickel anode decreased, and the character of the deposit gradually improved until a satisfactory one was obtained after the addition of 25 c.c. of 4N hydrochloric acid. The acid content of the electrolyte was progressively increased until it finally contained 17.52 gm. of HCl per liter.

III. THE FUNCTION OF BORIC ACID.

Edward Weston, of the Weston Electrical Instrument Co., of Newark, N. J., was the first to use boric acid in the nickel bath and he patented[44] its use in 1878. Since the expiration of the patent, its use has become very general in commercial plating. "He claims[45] that the addition of boric acid or its compounds prevents the deposition of sub-salts upon the cathode, renders the solution more constant and stable in composition, diminishes the liability to the evolution of hydrogen, permits the use of a more intense current, and improves the character of the deposit by rendering it less brittle and by increasing the tenacity with which it will adhere to a metal surface."

Langbein[46] states that "the action of boric acid has not yet been scientifically explained, but numerous experiments have shown that the deposition of nickel from nickel solution containing boric acid is neither more adherent nor softer and more flexible than that from a solution containing small quantities of a free organic acid. Just the contrary, the deposition is harder and more brittle in the presence of boric acid * * *. It has a favorable effect upon the pure white reduction of the nickel, especially in the nickeling of rough castings."

Bennett,[47] in discussing the paper of Kalmus on the electrodeposition of cobalt, says, "The solution of cobalt sulphate, which contains only a little greater quantity of cobalt, can be run at much higher rates of deposition in the presence of sodium chloride and boric acid. Since it seems to be impossible to get the people who are interested in nickel plating to explain the effect of such additions, it appears to me that Mr. Kalmus would advance our

[44] U. S. Patent, 211071, Dec. 17, 1878.
[45] Watts, Trans. Amer. Electrochem. Soc., 23, 132 (1913).
[46] Electro-deposition of Metals (1909), p. 249.
[47] Trans. Amer. Electrochem. Soc., 27, 118 (1915).

knowledge of electro-deposition, and, furthermore, score heavily on the nickel people, if he would determine what the specific action of boric acid and sodium chloride is."

Quite recently the *Brass World*[48] published an article by E. S. Thompson, purporting to give an explanation of the function of boric acid. That the article was written by one who is evidently unacquainted with even the rudiments of chemistry and electricity is shown by the following excerpt: "We will consider a solution composed of nickel sulphate, sodium chloride and boric acid. As the electric element forces oxygen out at the anode it necessarily forms a new combination with the hydrogen, and perhaps the nickel. But as we have boric acid there as a catalytic agent, it takes charge of the electric current and forms a combination without itself undergoing decomposition, and forces the sulphuric acid out of its combination with nickel. The chlorine which has been forced out of the sodium rushes in to take the place of the boric acid and forms chloride of nickel, having electro-hydrogen (we will call it that) as its solvent. * * *. The oxygen is forced out of the solution at the anode, its volume being exactly equal to the volume of electricity which has entered the solution. Then the boric acid takes charge of the electricity for an instant and forms a combination with the nickel sulphate. * * *. It will be seen by this that the handling of these solutions must be done by a man who understands their actions."

Having succeeded in securing satisfactory deposits of nickel from electrolytes containing small concentrations of the inorganic and organic acids, it seemed probable that the action of boric acid was simply to maintain a faint acid reaction in the electrolyte, which is a condition essential to a good deposition of nickel. The data which support this view are given as follows:

A bath consisting of 120 gm. per liter of nickel sulphate was prepared, neutralized with nickel carbonate and "aged" for 24 hours at a low current density. This solution was neutral to litmus. Using a copper cathode, current densities from 0.6 amp. to 3 amp. per sq. dm. were employed, but a satisfactory deposit was not obtained. At the lower current densities the deposit was black and rubbed off, while at the higher current strengths there was a coating on the cathode of a salt of a light green color. However,

[48] Brass World, 12, 37 (1916).

a bright, adherent deposit was obtained upon the addition of 0.25 percent of sulphuric acid.

Again, an electrolyte was prepared which had the following composition:

$NiSO_4.6H_2O$	120 gm.
$NiCl_2.6H_2O$	10 "
K_2SO_4	2.5 "
H_2O	1000 cc.

Upon electrolyzing at various current strengths with a copper cathode no satisfactory deposit was obtained. Another electrolyte was prepared of similar composition except that potassium hydrogen sulphate was substituted for the normal salt, and fine, bright, adherent deposits were obtained at current densities of 0.5 amp. and 1 amp. per sq. dm. Higher current densities gave unsatisfactory deposits.

A bath was made by digesting a saturated boric acid solution with nickel carbonate until the resulting solution was neutral to litmus. Electrolyzing at three different current strengths, the deposits were all dull gray and non-adherent, but upon adding boric acid to a concentration of 30 gm. per liter, a fine metallic, adherent deposit resulted. Again a solution containing 120 gm. per liter of nickel acetate failed to give a good deposit, but upon acidifying with 0.25 percent of glacial acetic acid, a fine, metallic, adherent deposit was obtained. Likewise, an electrolyte consisting of 120 gm. of nickel chloride per liter gave deposits which were black and non-adherent, but upon the addition of 9 c.c. of 4N hydrochloric acid, a bright, adherent deposit was produced. Neutral potassium tartrate added to a solution of nickel sulphate does not cause a good deposit, but the addition of potassium hydrogen tartrate gives a fine deposit.

A solution consisting of 120 gm. of nickel sulphate and 10 gm. of nickel chloride per liter was prepared, but it failed to give a good deposit at several different current densities. This solution was then acidified separately with sulphuric, boric, acetic, lactic, nitric, phosphoric, oxalic, tartaric, citric, succinic, benzoic, salicylic and hydrochloric acids. From each different bath a good deposit was obtained. In the case of the benzoic and salicylic acids the solutions were prepared by adding the required amount

of nickel sulphate to water saturated with respect to the acid at room temperature. Indeed, in so far as the electrolyte is concerned, a nickel sulphate solution acidified with hydrochloric acid contains all the factors necessary for a good nickel deposit. There is chloride to insure good anode corrosion, and acid to promote a bright, adherent deposit. In fact, such a solution gave fine, adherent deposits at current densities varying from 0.7 amp. to 2 amp. per sq. dm.

The results of these experiments are very interesting. An acid reaction to the electrolyte is necessary for a good deposit of nickel, since those baths which were neutral in reaction all failed to give a good deposit. Since good deposits were secured from solutions acidified separately with sulphuric, boric, lactic, acetic, nitric, phosphoric, oxalic, tartaric, citric, succinic, benzoic, salicylic and hydrochloric acids, it is demonstrated that boric acid has no function in the electrolyte which is different from that of any other acid. It simply maintains in the electrolyte a small concentration of acid, which is necessary to secure a good deposit. Owing to the fact that it is fairly soluble, and to the fact that it is a very weak acid, it lends itself to practical use better than most of the acids listed above. To show how weak boric acid is, it is only necessary to recall the well-known fact that a solution saturated with boric acid at room temperature may be dropped into the eye with impunity. Boric acid, then, simply acts in the capacity of a reservoir for keeping up a constant but small concentration of hydrogen ions in the electrolyte. In so far as their effect on the properties of the deposited nickel is concerned, hydrochloric or sulphuric acid could be substituted for the boric acid, but since the hydrogen ions in the electrolyte are gradually plated out, these strong acids, at the concentrations which must be employed, are already completely ionized and so cannot furnish more hydrogen ions to the electrolyte as the very weak boric acid can do. In this fact lies the only difference in the function of boric, sulphuric or hydrochloric acids in the plating bath, except that, in the case of hydrochloric acid, the chloride increases anode corrosion.

In a recent paper, Mathers[49] has recommended a nickel bath of the following composition:

[49] Trans. Amer. Electrochem. Soc., 29, 383 (1916).

$NiSO_4.(NH_4)_2SO_4.6H_2O$	40	gm.
$NiSO_4.6H_2O$	120	"
H_3BO_3	20	"
$MgCl_2.6H_2O$	20	"
$(NH_4)_3C_6H_5O_7$	3	"
H_2O	1000	cc.

The maximum current density that could be used was 1.6 amp. per sq. dm. It seems that this bath is more complex than necessary. Better conductivity is obtained by adding nickel ammonium sulphate, but this results in a lowered nickel content, which does not permit the bath to be operated at a current density higher than 1.6 amp. Magnesium chloride insures proper anode corrosion, but it would be better to substitute nickel chloride for this purpose in order not to decrease the nickel content. Ammonium citrate is added to prevent the formation of basic compounds from iron in the so-called "soft" anodes, but when chloride is present, it is unnecessary to employ such anodes, as pure nickel anodes would corrode properly.

For general purposes a bath of the following composition is proposed:

$NiSO_4.6H_2O$	240	gm.
$NiCl_2.6H_2O$	15	"
H_3BO_3	30	"
H_2O	1000	cc.

These salts are readily soluble at ordinary temperature and the boric acid may be readily dissolved by raising the temperature of the water slightly, although the acid will dissolve at room temperature. At this temperature the bath may be operated at any current strength between 0.5 amp. and 10 amp. per sq. dm., and by raising its temperature to 75°, it is possible to employ current densities as high as 33 amp. per sq. dm., as Watts[50] has recently demonstrated. At room temperature the specific resistance of this electrolyte is 23.54 ohms per centimeter cube, while that of Mathers' bath is 24.56 ohms.

In the same paper Mathers[51] states that "citric, acetic or benzoic acids cannot be used in the place of boric acid." If this statement means that good deposits of nickel cannot be obtained from electrolytes acidified with these acids, then the writer cannot

[50] Trans. Amer. Electrochem. Soc., 29, 395 (1916).
[51] Trans. Amer. Electrochem. Soc., 29, 383 (1916).

concur in it, as excellent deposits were obtained from baths acidified separately with all these acids as well as with salicylic acid. At first, trouble was experienced in getting an adherent deposit from the benzoic acid bath, but the trouble was traced to the fact that the copper cathode was being subjected too long to the action of the electric cleaner. When it was allowed to stay in the cleaner for about ten seconds, a bright, adherent deposit was obtained from the benzoic acid bath.

Bennett[52] states that "nickel cannot be deposited from an acid solution," and later explains that although the body of the electrolyte may be acid in reaction, yet to secure a good deposit the film of solution next to the cathode must be alkaline. He further explains that the hydrogen liberated during the electrolysis of an acid solution "leaves the hydroxyl ion from the water in slight excess at the cathode." The concentration of hydroxyl ions that serves to maintain equilibrium conditions in water is, at best, very small, and when this very small concentration of hydroxyl ions is further reduced by the addition of a strong acid, such as hydrochloric or sulphuric, it is hard to believe, from theoretical considerations, that the minutely small concentration of hydroxyl ions, which maintains equilibrium conditions, could play any important part in causing a good deposition of nickel. Thus, from theoretical considerations, the hypothesis that a film of electrolyte, alkaline in reaction next to the cathode, is a condition necessary to secure a good deposit of nickel is untenable and, practically, it is well known that the electrolyte must be slightly acid in reaction to secure the same result.

SUMMARY.

1. A study of the corrosion of cast nickel, electrolytic nickel, and annealed electrolytic nickel anodes has been made in the following electrolytes: nickel sulphate solution; nickel sulphate solution to which boric acid was added; nickel sulphate boric acid solution to which various amounts of nickel chloride were added.

2. Measurements of the total polarization pressures and current efficiency tests of these three anodes in the electrolytes listed above have been made.

[52] Trans. Amer. Electrochem. Soc., 25, 338 (1914).

3. A study has been made of the conditions necessary for the direct electro-deposition of nickel on zinc, together with some of the electrolytes which have been proposed for this purpose.

4. Nickel can be deposited directly on zinc from baths used to deposit nickel on more electro-negative metals by employing a higher initial current density than is used with the more electro-negative metals.

5. Nickel has been deposited directly on zinc from an approximately half normal hydrochloric acid solution to which 120 gm. per liter of nickel sulphate were added.

6. The beneficial action of sodium citrate in the baths for the direct nickeling of zinc has been found to consist not in changing the potential of zinc but in decreasing the rate of deposition by immersion. Sodium potassium tartrate and sodium malate have a similar action but they do not permit the use of as high a current density as the citrate bath.

7. A new bath for the rapid and direct nickeling of zinc is proposed.

8. The use of pure nickel anodes and the use of nickel chloride to secure anode corrosion, instead of any other chloride, is advocated.

9. The use of nickel sulphate in the electrolyte instead of nickel ammonium sulphate is advocated.

10. The function of boric acid in the electrolyte has been explained.

In conclusion, the writer desires to express his appreciation of the assistance given him by Dr. O. P. Watts during the progress of the work reported in this paper.

Laboratory of Applied Electrochemistry,
University of Wisconsin,
May, 1916.

DISCUSSION.

G. B. Hogaboom: I would like to speak upon this paper, primarily in the way of making a plea for the members of the American Electro-platers Society. The author in the first paragraph acknowledges that nickel plating is not practiced by those

who are thoroughly familiar with the fundamental principles of chemistry and electricity, and then writes a paper in the most technical terms.

This is a paper for the electro-chemist, and loses a great deal of its value to the nickel-plating industry on account of its highly technical character and because all of the measurements are given in the metric system.

The author makes the statement in the paper that although nickel plating has been practiced for about fifty years, it is still based upon "cut and dried" methods. That puts me in mind of Elijah when he said that he "alone was left to represent the children who worshipped and feared God"; because if he had looked around he would have seen that there are a great number of the larger plants which are carrying on nickel plating on scientific principles, and the art is progressing very well along that line.

On page 107, speaking about the presence of iron, tin and carbon in the solution, he says: "Although solution of anode is promoted by such a practice, serious troubles result." I have seen solutions that have been in use for twenty-five years and were still being used, without any serious trouble following. In practice this statement is disproved.

If the author was familiar at all with the nickel deposits, he would know that a small percentage of copper in nickel will cause a black deposit.

I had occasion to look over some deposits of nickel on highly polished steel that were peeling, the solution was quite acid from the addition of an excess of boric acid. A nickel deposit that peels on account of it being acid from sulphuric acid, if crushed in the hand, will cry like tin. A deposit that peels from boric acid will crumble up in your hand and will not cry at all.

Leonard Waldo: I note one thing on page 126, an article published in the "Brass World" is very sharply criticised. I notice the edition of the "Brass World" in which the criticism occurs is the twelfth volume, 37 something, in the year 1916. The paper proceeds to criticise the article which was published in the "Brass World," and I attribute the inaccuracy of the "Brass World," in this instance, to the decease of that brilliant brass and copper metallurgist, Irwin Starr Sperry, its former editor.

C. G. FINK: It is gratifying to hear that the "Brass World" has taken the lead in using both systems of measurements, and I hope the "Metal Industry" will soon follow suit. I wonder whether our Society could not induce the "Metal Industry" to adopt the metric system at least partially, adding the metric system in parenthesis with the present English system. This procedure would make it so much easier for the chemist, who is not a plater, to read the plater's article. It is more difficult to comprehend "ounces of silver per barrel" than "grams per litre."

L. D. HAMMOND (*Communicated*): Mr. Hogaboom is quite correct in his statement that this is a paper for the electro-chemist, but it is to be regretted that the only thing he got out of it was the impression that I had set myself up as an Elijah. In this connection, however, it may be well for him to recall that it was Elijah who pointed out to his people the mistakes they were making, and that Elijah's work was constructive. Experience has shown that the plater is not independent of his scientifically trained brother, and the electro-chemist has much to gain from the helpful suggestions of his more practical brother. The chasm that separates the practical man from the theoretical one must be bridged by the real Elijah of the situation, who will be the college-trained man with an apprenticeship in the practical field. Such a man would interpret to workers in the practical field anything of interest and value to them in a technical paper instead of dismissing it with the statement that the author assumes unto himself the rôle of an Elijah. The electro-chemist and electroplater must work hand in hand and it is to be regretted that my paper was interpreted in any other way by the representative of the platers.

Mr. Hogaboom asserts that he knows of plating solutions which have been used for twenty-five years without any serious trouble following. It seems to me he is looking at the problem from the standpoint of the practical man who is interested only in securing a good deposit on the article to be plated. But what of the efficiency of anode corrosion, and what of the efficiency of deposition at the cathode? Did the article show signs of rusting sooner or later from the iron deposited along with the nickel? These are questions which must be considered as well as the character of the deposit.

As to Mr. Hogaboom's reference to the effect of a small percentage of copper in nickel deposits, his remarks are entirely gratuitous so far as my paper is concerned, as the only statement I made in regard to this matter was to quote others, including Mr. Hogaboom himself.

I was pleased to receive from Mr. Waldo an explanation as to why that article on the function of boric acid in the nickel bath was ever published in the "Brass World." The editorship of the trade journals is another field requiring the services of the new Elijah—the college man with a practical training.

In view of Mr. Hogaboom's criticism that all the measurements are given in the metric system, it is interesting to learn from Mr. Fink that the "Brass World" is doing pioneer work in introducing into its columns the use of the metric system, and to learn, as well, that he hopes the "Metal Industry" may be induced to do likewise. It is hard to break away from a long-established habit, but the universal use of the metric system is coming, and the wise practical man will prepare himself accordingly. And once he becomes accustomed to its use I imagine he will often wonder why we have endured our present cumbersome system of weights and measures so long as we have.

A paper presented at the Thirtieth General Meeting of the American Electrochemical Society, held in New York City, September 28, 1916, Mr. L. E. Saunders in the Chair.

CURRENT EFFICIENCIES IN NICKEL PLATING BATHS WITH ROTATING CATHODES.

By F. C. Mathers and E. G. Sturdevant.

This paper shows that the low current efficiencies in nickel plating with rotating cathodes are due to impurities in the solution. The presence of anything that can lower the current efficiency will have a greater action for a shorter time in the bath with the rotating cathode than with a stationary cathode, because the stirring will bring the cathode in contact with more of the solution. Calhane and Gammage,[1] who first experimented with rotating cathodes in nickel baths, gave no explanation for the lower yields which were 12 percent, in some cases, compared with 90 percent using stationary cathodes.

Bennett, Kenny and Dugliss[2] formulated the theory that the rotation of the cathode prevented the formation over the cathode surface of an alkaline film of ammonium hydroxide which was necessary for a high yield. This theory is untenable as shown by the yields with stationary and with rotating cathodes, becoming practically equal in value with baths that are sufficiently pure.

In a more recent paper, Bennett, Rose and Tinkler[3] advanced the theory that the free acid or the hydrogen ions in the baths was the cause of the low yields, and that the yield with the rotating cathode was lower than with the stationary one, because the acid or the hydrogen ions in the bath was more rapidly brought up to the cathode. This theory was based upon experiments in which the addition of ammonium hydroxide was found to increase the yields with both rotating and stationary cathodes, but the yields with the rotating cathodes were always lower except in one case. The addition of the ammonium hydroxide initially in-

[1] J. Am. Chem. Soc., **29**, 1268 (1907).
[2] Trans. Am. Electrochem. Soc., **25**, 335 (1914).
J. Phys. Chem., **18**, 373 (1914).
[3] Trans. Am. Electrochem. Soc., **28**, 339 (1915).
J. Phys. Chem., **19**, 564 (1915).

creased the yields somewhat, but continuous electrolysis or aging produced further gradual increases in the yields with both rotating and stationary cathodes. This agrees with the theory that impurities which cause the low yields are gradually eliminated during electrolysis. If the lower yields which they obtained with the rotating cathodes were due to the more rapid bringing up of hydrogen ions, it follows that the addition of sufficient ammonium hydroxide should have eliminated the hydrogen ions and thus made the yields with both rotating and stationary cathodes the same. No such place was found. With larger amounts of ammonium hydroxide (10 cc. of 1:10 in 120 cc. of bath), the yields decreased with both stationary and rotating cathodes. If these experimenters had used larger volumes of solution, greater variations would have been found. As it was, the 120 cc. of solution very soon became purified by the electrolysis.

MANIPULATION.

Each experimental bath contained 24 grams of nickel ammonium sulphate, 3 grams of nickel chloride and 300 cc. of water. The nickel ammonium sulphate was a commercial preparation, bought from a plating supply house. The nickel chloride was a Schuchardt preparation. Two anodes made of pieces of nickel, stripped from electrolytic cathodes, were used in each bath, one on each side of a beaker. The total exposed area of the two anodes (not counting the surfaces towards the beaker) was about 53 sq. cm. (8.2 sq. in.). The anodes were suspended by lead strips or wires. The stationary cathodes were made of sheet copper, and each had a total area of 50 sq. cm. (7.7 sq. in.). The moving cathode, a copper rod having a surface in the electrolyte of 9 sq. cm., was rotated 2,200 revolutions per minute. A current of 0.2 amp., which was used in each case, gave a current density of 0.4 amp. per sq. dcm. (3.7 amp. per sq. ft.) with the stationary cathode and 2.2 amp. per sq. dcm. (20.6 amp. per sq. ft.) with the rotating cathode. The use of a larger or a smaller current density was found to have a negligible influence within experimental errors. Each bath was run for one hour with a stationary cathode and then one hour with a rotating cathode, a deposit of about 0.22 gram of nickel being obtained in each case. A copper coulometer was run in series with each

experiment. The bath was then electrolyzed continuously or aged with stationary electrodes and a current of 0.2 amp. until another quantitative determination was desired, at which time a run was made with the stationary and with the rotating cathode as before. In this way the determinations of the yields at intervals showed the effect of electrolysis on the elimination of the impurities in the bath. Since yields with stationary and rotating cathodes were run in each bath, any variation in the bath itself did not affect the comparison of the two values. The age of a bath in the following tables means the number of hours that the bath had been electrolyzed or aged at the time the determination was started.

Bath No.	Age in hours.	Current efficiency.	
		Rotating cathode. Percent.	Stationary cathode. Percent.
1	0	76.4	89.4
	3	91.9	92.2
	15	90.5	92.9
2	0	77.6	91.9
	3	87.7	93.2
	15	91.0	95.6
3	0	79.6	92.6
	3	89.8	90.9
	15	92.6	93.5
	7	93.4	94.9
4	0	82.2	88.1
	7	87.1	94.9
	23	97.6	98.6
	32	98.2	99.5
5	0	84.5	92.4
	17	97.2	98.7
	33	96.8	99.2
	60	96.5	99.2
6	0	86.3	92.7
	13	90.7	97.1
	35	96.4	100
	66	95.5	99.4
7	0	84.2	90.2
	17	91	98.7
	59	97.2	100

ADDITION OF REAGENTS TO NEUTRALIZE THE ACIDITY IN THE BATHS.

Bath 1 was untreated, 2 was boiled with freshly precipitated nickel hydroxide for ten minutes, 3 was treated with 1 cc. of 1 : 10 ammonium hydroxide, an additional 1 cc. being added be-

fore each of the subsequent runs, making a total of 4 cc. for the final determination, 4, 5 and 6 contained 1, 3 and 5 percent[4] of borax respectively, and 7 was boiled for ten minutes with nickel borate.

In all cases the yields gradually increased as the baths became older. On the same bath the yields were lower with the rotating than with the stationary cathode. The logical conclusion is that free acid is not the cause of the low yields, otherwise these neutralizing substances, having removed the free acid, would have made the yields on the initial runs as high as after hours of electrolysis. Moreover, the addition of 2 cc. of 1:10 ammonium hydroxide just before electrolysis lowered the yields to 86.4 percent (s) and 76.9 percent (r) yet the bath was alkaline to litmus. It should be noted that the baths containing the borax very rapidly increased in efficiency during aging. The gradual increase in yields with aging is easily explained by the assumption that the impurities causing the low yields were gradually eliminated during the electrolysis. If free acid had been causing the trouble the yields would have gradually increased just as they did, the acid being exhausted during the electrolysis, yet the idea is unreasonable that any free acid could have been present in the baths after treatment with the neutralizing agents that were used. Apparently the nickel salts used in this work contained very little free acid, as is shown by the yields from the untreated bath being practically equal to those from the neutralized baths. The authors were unable to obtain bright adherent deposits from solutions containing 5 cc. or 10 cc. of 1:10 ammonium hydroxide, although Bennett and others show curves from these alkaline baths. It is well known that good nickel deposits cannot be obtained from baths that are alkaline to litmus.

TEST OF THE EFFICIENCY OF NICKEL HYDROXIDE IN NEUTRALIZING FREE ACID IN THE BATH.

Two baths that had been aged until high yields had been obtained were treated with sulphuric acid, which immediately lowered the yields. The baths were then boiled for ten minutes with nickel hydroxide, filtered and cooled. They then gave almost the same high yields that they did before the addition of the sul-

[4] Percent in this paper means grams per 100 cc.

phuric acid. This showed that the nickel hydroxide completely neutralized the free sulphuric acid. The conclusion follows that a low yield in any bath which has been boiled with nickel hydroxide is caused by something other than free mineral acid. Moreover, the data show that the yields immediately start at a high value if the impurities in the bath have once been removed. The data on the two baths are as follows:

Treatment of bath.	Current efficiencies in percent in bath with			
	5 percent boric acid.		No boric acid.	
	Stationary.	Rotating.	Stationary.	Rotating.
Yield after aging but before addition of sulphuric acid.....	98.6	96.2	98.	95.3
After adding 25 drops of concentrated sulphuric acid.....	76.9	58.9	62.9	55.9
After boiling for 10 min. with nickel hydroxide and filtering..	96.9	93.7	98.5	96.9

The boric acid in some way prevented the yield from immediately returning to the value that was obtained before the addition of the sulphuric acid.

ADDITION OF BORIC ACID.

The baths were boiled with nickel hydroxide to neutralize any free acid, and were filtered before the boric acid was added.

Percent of boric acid.	Age.	Current efficiency in percent.	
		Stationary cathode.	Rotating cathode.
1	0	90.1	82.6
1	9	95.6	90.8
1	36	97.4	91.7
1	68	99.1	98.7
2	0	92.3	79.7
2	20	98.0	95.4
2	36	98.4	96.9
3	0	91.4	81.1
3	35	95.9	81.2
3	57	98.0	95.3
3	77	98.3	95.5
4	0	87.1	80.3
4	32	95.6	94.5
4	70	95.7	95.6
4	110	94.4	90.8

These data show that the free boric acid decreased the yields in a marked degree only when a concentration of 5 percent or more was used. In all cases the yields gradually increased as electrolysis continued. Boric acid is weakly dissociated, hence it would not be expected to reduce the yields like a mineral acid.

ADDITION OF IMPURITIES TO THE BATHS.

Iron. All nickel anodes contain iron as an impurity in quantities varying from 8 percent in the cast nickel anodes to almost traces in the electrolytic cathodes which were used in these experiments. Any decrease in the yield produced by the iron is the result of oxidation by the air to ferric, with later reduction at the cathode to ferrous. If the iron which dissolves from the anodes as ferrous remained in this condition and was deposited as such, any effect on the yield would be practically negligible because the electrochemical equivalents of nickel and ferrous, 29.3 and 27.9 respectively, are so nearly the same. A bath to which 2 percent of ferrous sulphate was added gave yields of 93.6 (s) and 86.9 (r) for the initial determination. The yields increased to 99.7 (s) and 97.1 (r) after continuous electrolysis for 94 hours. The cathodes were dark in color and contained much iron. With 4 percent ferrous sulphate, the yields started lower, 83.7 (s) and 46.7 (r) and decreased to 48.9 (s) and 40.2 (r) after 43 hours. A large quantity of precipitate formed in the bath which probably became acid as a result of the hydrolysis. The first cathode contained 39 percent of iron.

The addition of 0.33 percent of ferric ammonium sulphate to a bath that had been aged until yields of 96.3 (s) and 93.2 (r) were obtained, immediately lowered the yields to 91.4 (s) and 81.1 (r). The salts used in making a bath contained iron equivalent to 0.02 gm. of ferric ammonium sulphate, hence only a small portion of the reduction in yield in a regular bath can be attributed to the iron in the salts used or in the pure electrolytic nickel anode material. The iron in ferro-nickel anodes is sufficient to reduce the yields in stirred solutions where the conditions for oxidation are favorable.

Nitrates. The addition of 0.05 gm. of potassium nitrate to a bath that had been aged until it was giving yields of 99.9 (s) and 97.2 (r) lowered the yields as follows:

Age.	Current efficiencies.	
	Rotating.	Stationary.
0	76.2	88.7
4	88.5	91.5
9	89.0	94.1

The analysis of the nickel chloride used in this work showed nitrate equivalent to 0.025 gm. of potassium nitrate in 3 gm. of the nickel chloride, the quantity used in a bath. Only traces of nitrate were found in the nickel ammonium sulphate. These results show that nitrate is the impurity that is responsible for a large part of the initial depression in the current yields.

Organic Salts. Ammonium citrate and ammonium acetate each produced a lowering of the yields as shown by the following tables:

Percent of ammonium acetate.	Percent of ammonium citrate.	Age.	Current efficiencies in percent.	
			Stationary cathode.	Rotating cathode.
	1	0	83.8	91.8
	1	20	77.2	88.2
	1	40	50.0	79.0
	1	58	50.8	83.8
	3	0	81.9	88.5
	3	18	59.9	82.8
	3	34	81.9	87.7
	3	80	75.1	85.0
	5	0	60.4	81.5
	5	20	72.6	85.5
	5	52	79.7	84.3
	5	80	63.3	77.6
1		0	92.1	94.7
1		8	94.6	95.4
1		12	94.9	95.2
1		20	96.1	96.4
2		0	88.3	93.8
2		8	95.0	97.7
2		12	96.3	96.0
2		20	86.9	99.0
4		0	62.3	82.8
4		8	84.3	89.3
4		12	76.2	90.0
4		20	79.6	90.1

The baths with the ammonium citrate finally became alkaline during the course of the electrolysis, which accounts for the low

results finally reached. Very small amounts of these organic salts did not produce appreciable lowering of the yields, hence it is thought that the traces of organic matter[5] in the nickel salts contributed only slightly to the lowering of the yields.

BATHS PREPARED FROM PURIFIED SALTS.

Baths prepared from purified salts gave initially high yields. The nickel ammonium sulphate was prepared by three crystallizations of the salt obtained from some old baths that had been aged until high yields were obtained. The nickel chloride was purified by electrolyzing a solution of nickel chloride with electrolytic nickel anodes for fifty hours. The nickel chloride from this solution was then crystallized twice. The nickel chloride which seemed to contain most of the harmful impurities was the most difficult salt to purify on account of its great solubility. Potassium chloride (C. P.) in place of the nickel chloride gave high yields. The following table shows the results:

Percent.		Age.	Current efficiency in percent.	
Nickel chloride.	Potassium chloride.		Rotating cathode.	Stationary cathode.
3		0	96.0	96.5
3		15	96.3	99.1
3		30	96.9	99.0
	3	0	96.1	97.6
	3	15	98.2	98.8
	3	30	98.2	99.4

The increase in yields from these baths as aging progressed showed that the salts were not entirely pure. Also the higher yields from the potassium chloride bath showed that it was purer than the nickel chloride.

VOLUME EFFECT.

It has been observed[6] that the larger the volume of the electrolyte in silver coulometers, the heavier the deposit of silver. This "volume effect" was shown[7] to be due to impurities by the fact that the weight of deposit was independent of the volume if the electrolyte was sufficiently pure. This gives an excellent

[5] Calhane and Gammage (1) reported organic matter as one of the impurities in nickel ammonium sulphate.
[6] Rayleigh, Phil. Trans., **175**, 411 (1884).
[7] Rosa, Vinal and McDaniel, Bull. Bur. Std., **9**, 516 (1913).

method of demonstrating the effect of impurities on the efficiency of nickel deposition. Three nickel baths of 100, 200 and 300 cc. were prepared from the same salts and in exactly the same way. These baths were electrolyzed continuously with rotating cathodes and the deposits were weighed each hour. The data are as follows:

Age.	Efficiencies in percent.					
	100 cc. bath.		200 cc. bath.		300 cc. bath.	
	Rotating.	Stationary.	Rotating.	Stationary.	Rotating.	Stationary.
0	85.8	....	83.3	....	74.2	....
1	94.2	....	92.8	....	87.9	....
2	97.8	....	93.4	....	91.1	....
3	97.8	....	....	....	95.0	....
4	....	96.9	97.5	....	....	....
5	....	....	97.6	....	97.8	....
6	....	....	....	97.3	....	96.5

The data show that it required about twice as long for the 200 cc. bath and almost three times as long for the 300 cc. bath to reach an efficiency of 97.8 as in the case of the 100 cc. bath. The area between each curve and a line parallel to the abscissa at 97.6 percent was 1.82, 3.59 and 6.82 respectively for the 100, 200 and 300 cc. baths. These numbers, which represent the total depression of the efficiencies by the impurities in each bath, should stand in the same ratio as the volumes of the baths, which they do approximately. A determination, made with a stationary cathode as soon as the efficiency had reached 97.6 percent, gave a result in every case equal within experimental error to the efficiency with a rotating cathode. This shows conclusively that any difference between the two must be due to impurities and not to any specific action of the rotation or agitation of the solution.

An additional confirmation of the theory was obtained by repeating the above experiments with 100, 200 and 300 cc. baths prepared from purified salts. The current efficiencies in all of them for the first hour were approximately the same, 98 percent. This shows that there is a volume effect only when impurities are present.

The continuous electrolysis with rotating cathodes removed the

impurities quicker than with stationary cathodes. Some impurities remained in a bath even after many hours of electrolysis with a stationary cathode, hence a rotating cathode in such a bath gave a lower yield than with a stationary cathode, because the agitation of the solution brought the remaining impurities to the cathode. It was not feasible to age all of the baths with rotating cathodes hence in most of the tables the stationary cathodes show the higher values.

SUMMARY.

This paper shows that the impurities in the nickel salts are the cause of the low initial current yields with stationary cathodes and the still lower yields with rotating cathodes. The following points are brought out:

1. Free mineral acid can produce this lowering of the yields, but the neutralization of the baths by boiling with nickel hydroxide did not overcome the trouble.

2. The yields from baths electrolyzed continuously with rotating cathodes started low but reached values of about 97.6 percent in 2, 4 and 5 hours respectively for baths of 100, 200 and 300 cc. made from commercial nickel salts. Similar baths made from purified salts gave yields of about 98 percent for the first hour regardless of the volume. This shows that impurities produce all the lowering of the yields.

3. The yields with stationary and with rotating cathodes are approximately equal in all cases where the baths are sufficiently pure. Nitrate lowered the yields more than any other impurity that was tried. Ferric salts, ammonium citrate or ammonium acetate lowered the yields, but ferrous sulphate up to 2 percent was almost without effect.

4. Free boric acid lowers the yields somewhat when present in quantities greater than 2 percent.

Indiana University, Bloomington, Ind.

A paper presented at the Thirtieth General Meeting of the American Electrochemical Society, held in New York City, September 28, 1916, Mr. L. E. Saunders in the Chair.

THE PROTECTION OF IRON BY ELECTROPLATING.

By Oliver P. Watts and Paul L. DeVerter.

Although nickel-plated iron is satisfactory for use indoors, when exposed to the weather it almost invariably rusts. Brass-plated steel is extensively employed for the cheaper grades of builders' hardware, but is even more unsatisfactory than nickel plate for out of door use. In reply to an inquiry concerning the possibility of a durable brass plate on steel for use out of doors, *The Metal Industry*[1] says, "An electro-deposit of zinc on steel or iron is the only one that will withstand atmospheric conditions for any length of time, and a demand is now being made for hardware that has received an electro-deposit of zinc before being plated with any other metal for ornamental purposes, such as nickel, copper, brass or bronze. This double coating gives good service and is the only satisfactory one for hardware which is exposed to the weather."

The superior protective action of electro-galvanizing in comparison with deposits of other metals on iron is well recognized. This has generally been ascribed to voltaic action; whenever a hole is broken or worn through the plating a voltaic cell is formed between the metallic coating and the exposed iron. If the coating consists of a metal which is electro-positive to iron, the latter is cathode and is protected from corrosion, but if the coating is electro-negative to iron this becomes anode, and is corroded worse than if the "protective coating" were entirely absent. Examination of tables of potentials of the metals shows that, of the metals which can be satisfactorily plated out of aqueous solutions, only zinc and cadmium are electro-positive to iron. Since cadmium is not used for commercial plating on account of the expense, zinc remains as the only electroplate which can protect iron by voltaic or galvanic action. Theory and practice appear to be in harmony.

[1] Metal Industry, 1915, p. 469.

Galvanic action requires that two unlike conductors be in electrical connection with each other and with an electrolyte. So long as the iron is completely covered by the electroplate there is no opportunity for voltaic action, either corrosive or protective, and, so far as rusting of the iron is concerned, it is immaterial what metal constitutes the coating. The protection of iron by deposits of zinc and its universal rusting when plated with other metals seems to indicate either that electro-deposits of zinc are less porous than those of other metals, or that in the thickness used commercially all electro-deposits are porous, or on exposure soon become so, and thus the superior protection by zinc is due solely to its galvanic action.

To investigate the porosity of electroplating, and to determine the protection afforded to iron by deposits of different metals, a series of experiments has recently been carried out in the electrochemical laboratory of the University, and it is thought that these are of sufficient interest to electroplaters to merit publication.

THE PROTECTION OF IRON BY DEPOSITS OF NICKEL, COPPER AND BRASS.

Since it is generally conceded that commercial plating with these metals does not protect iron from rust, it was decided to try much thicker deposits than those usually employed. A company which makes great quantities of an article in daily use by millions of people specifies ten milligrams of nickel per square inch as the minimum for good deposits, and fifteen for their heaviest plate. The latter corresponds to an average thickness of 0.00348 mm. or 0.000137 inches, and requires an hour at five amperes per square foot for its deposition. For indoor use this deposit stands well the constant handling to which these articles are subjected. The deposits of the tables which follow range from this thickness to ten and in a few cases even twenty times heavier.

Strips of sheet iron were pickled in sulphuric acid to remove scale, cleaned in the electric cleaner, dried, weighed, returned to the electric cleaner for a few seconds, rinsed, and hung in the plating bath. After plating the strips were reweighed, and the average thickness of the deposit calculated. The brass and copper deposits were made from hot cyanide baths containing caustic soda; the zinc solution consisted of the sulphate and a little chlor-

ide; the nickel was plated from a rapid solution recommended by the writer[2], which was used hot except for two samples. The conditions of deposition are given in Tables I to IV.

TABLE I.

Brass Deposits on Iron.

No.	Time Min.	Temp.	Amp./dm.²	Thickness Inches	m.m.	Amp. Hrs./dm.²	Cur. Eff. Percent
1	55	Hot	11.5	0.00028	0.0071	1.0	26.7
2	10	Hot	11.5	0.00061	0.0155	1.9	30.1
4	15	Hot	12.3	0.0008	0.0203	3.07	25.5
6	30	Hot	12.6	0.00228	0.059	6.3	33.1
7	60	Hot	8.75	0.00327	0.0832	8.75	33.9
41	150	Hot	8.0	0.00607	0.1543	20.0	34.5

TABLE II.

Copper Deposits on Iron.

No.	Time Min.	Temp.	Amp./dm.²	Thickness Inches	m.m.	Amp. Hrs./dm.²	Cur. Eff. Percent
36	3	Hot	7.32	0.00027	0.0069	.37	58.2
3	10	Hot	6.83	0.00096	0.0245	1.12	71.2
5	15	Hot	6.83	0.00099	0.0251	1.58	51.8
9	45	Hot	5.55	0.00129	0.0327	4.1	31.9
8	75	Hot	5.68	0.00271	0.0689	7.1	39.1
42	120	Hot	3.25	0.00248	0.063	6.5	33.1
46	180	Hot	3.27	0.00686	0.1745	9.81	60.8

TABLE III.

Zinc Deposits on Iron.

No.	Time Min.	Temp.	Amp./dm.²	Thickness Inches	m.m.	Amp. Hrs./dm.²	Cur. Eff. Percent
21	4	Hot	4.88	0.00019	0.0049	0.32	71.6
19	1	Cold	14.7	0.000196	0.0050	0.24	97.4
14	3	Cold	13.25	0.00043	0.0109	0.66	85.3
10	5	Cold	13.65	0.00077	0.0195	1.14	86.2
11	12	Cold	12.5	0.00103	0.0263	2.3	63.1
13	30	Cold	9.55	0.00237	0.0603	4.77	60.5
12	25	Cold	14.7	0.00266	0.0667	6.1	52.0

TABLE IV.

Nickel Deposits on Iron.

No.	Time Min.	Temp.	Amp./dm.²	Thickness Inches	m.m.	Amp. Hrs./dm.²	Cur. Eff. Percent
30	20	Cold	1.3	0.00016	0.0042	0.43	45.5
25	10	Cold	2.3	0.00022	0.0055	0.4	51.0
31	15	Hot	4.85	0.00069	0.0176	1.2	78.5
33	90	Cold	1.0	0.00091	0.0231	1.5	62.5
29	20	Hot	5.28	0.00102	0.0255	1.76	72.0
32	25	Hot	6.48	0.00146	0.0371	2.7	63.5
34	40	Hot	7.2	0.00249	0.0633	4.8	55.0
44	180	Hot	4.23	0.00598	0.152	12.75	48.1
45	165	Hot	5.56	0.00702	0.178	15.05	42.7

[2] Trans. Am. Electrochem. Soc. (1916) 29, 126.

The samples were placed in wood racks, exposed to the weather, and examined occasionally for their appearance in regard to rust. The results are shown in Tables V to VIII.

RESULTS OF WEATHERING.

TABLE V.

Copper-plated Iron.

No.	Amp. Hrs./dm.²	Thickness Inches	Days required for rusting Slight	Moderate	Very bad
36	0.37	0.00027	8	10	14
3	1.12	0.00096	47	73	88
5	1.58	0.00099	47	73	88
9	4.1	0.00129	47	73	88
8	7.1	0.00271	67	88	..
42	6.5	0.00248	No rust in 70 days.		
46	9.81	0.00686	No rust in 70 days.		

TABLE VI.

Brass-plated Iron.

No.	Amp. Hrs./dm.²	Thickness Inches	Days required for rusting Slight	Moderate	Very bad
1	0.98	0.00023	20	32	73
2	1.9	0.00051	46	73	88
4	3.07	0.00066	47	73	88
6	6.3	0.00228	53	73	88
7	8.75	0.00327	53	73	88
41	20.0	0.00607	Tarnished, but no rust in 70 days.		

TABLE VII.

Nickel-plated Iron.

No.	Amp. Hrs./dm.²	Thickness Inches	Days required for rusting Slight	Moderate	Very bad
30	0.43	0.00017	9	19	40
25	0.4	0.00022	9	19	40
31	1.21	0.00069	12	19	53
33	1.5	0.00091	19	40	73
29	1.76	0.00102	19	40	73
32	2.7	0.00146	Tarnished, but no rust in 122 days.		
34	4.8	0.00249	Tarnished, but no rust in 122 days.		
44	12.75	0.00598	Bright, not even tarnished in 70 days.		
45	15.02	0.00702	Bright, not even tarnished in 70 days.		

TABLE VIII.

Zinc-plated Iron.

No samples rusted in 122 days.

The most striking feature of the weathering tests is the complete protection against rust during four months of very wet weather afforded by electro-galvanizing less than 0.0002 inch thick,

while rusting occurred through deposits of copper 0.0027, of brass 0.00327, and of nickel 0.00102 inch in thickness. With thin plating rusting was serious and widely distributed, but on the thicker deposits it was confined to a few widely scattered spots. Although Nos. 42, 46 and 41 showed no signs of rust after seventy days exposure, they had tarnished so badly that all resemblance to the original copper or brass was lost. Specimens Nos. 44 and 45 not only were free from rust, but the nickel plate appeared as bright as when deposited.

DOUBLE PLATING.

In addition to the quotation already cited in favor of a coating of zinc under brass or copper plating on iron, the current issue[3] of *The Metal Industry* contains the following: "Neither copper, brass or nickel gives a successful coating upon steel that will resist atmospheric influence and prevent the formation of rust. The large hardware manufacturing companies have realized these facts and are at the present time giving their product a preliminary coating of zinc from an alkaline cyanide zinc solution which is followed by direct deposition of copper, brass or nickel, or coating the zinc with copper or brass and then nickel plating. This method is the most effective for all purposes of plating upon steel when exposed to dampness or the action of salt air."

In view of such favorable reports from practical platers concerning the protective effect of a deposit of zinc beneath copper or brass plate, it was deemed advisable to test such double plating. Specimens were therefore prepared as shown in Table IX.

TABLE IX.

Double Plating on Iron.

No.	Metal	Time Min.	Temp.	Amp./dm.²	Thickness Inches	Thickness m.m.	Amp. Hr./dm.²	Cur. Eff.
15	Zinc	3	Cold	14.35	0.00041	0.0104	0.72	70.2
	Copper	15	Hot	7.18	0.00107	0.0272	1.79	47.3
16	Zinc	1	Cold	12.95	0.00013	0.0034	0.21	86.3
	Copper	20	Hot	5.95	0.00145	0.0368	1.98	70.0
20	Zinc	3	Hot	4.88	0.00018	0.0045	0.24	87.3
	Copper	15	Hot	7.32	0.00119	0.0304	1.83	50.5
17	Zinc	1	Cold	13.85	0.000157	0.0040	0.23	85.8
	Brass	25	Hot	12.15	0.00327	0.0832	5.5	58.3
18	Zinc	3	Cold	12.27	0.00040	0.0102	0.61	85.6
	Brass	20	Hot	11.7	0.00186	0.0473	3.9	48.4

[3] June, 1916.

TABLE X.

Results of Weathering on Double Plating.

No.	Amp. Hrs./dm.²		Thickness Inches	Days required for rusting
17	0.23	Zinc	0.000157	53, slight; 70, six rust spots on one side.
	5.5	Brass	0.00327	
18	0.61	Zinc	0.00040	40, slight; 70, shows 25 rust spots.
	3.9	Brass	0.00186	
15	0.72	Zinc	0.00041	14, slight; 70, much rusted.
	1.79	Copper	0.00107	
16	0.21	Zinc	0.00013	20, slight; Zinc blistered and broken in 70 days, rusted in such spots.
	1.98	Copper	0.00145	
20	0.20	Zinc	0.00018	14, slight; 70, many blisters and rust spots.
	1.83	Copper	0.00012	
35	0.33	Zinc	0.00019*	73, slight; 122, eight rust spots.
	0.92	Copper	0.00062	
35a	0.33	Zinc	0.00019*	53, slight.
	0.92	Copper	0.00062	

* As the weights of these samples were not recorded the thickness of the deposits have been computed from the ampere hours by comparison with other deposits.

The results of weathering in Table X show slightly better protection by double plating than with the same total thickness of brass or copper alone; had the zinc deposits been free from blisters it is probable that the results would have been still more favorable to the double deposit. The final rusting of every sample of double plating is in marked contrast to the complete protection afforded by zinc alone.

The zinc in No. 17 is nearly as thick as in Nos. 19 and 21, which gave perfect protection. The result of covering the zinc in No. 17 with 0.003 inch of brass has been to nullify the protective action of the zinc and to induce rusting at nearly the same rate as Nos. 6 and 7, which were without the coating of zinc. A detailed comparison of the other double deposits with the single coatings leads to a similar conclusion: the protective effect of the zinc coating is almost, if not completely, nullified by plating it over with brass or copper. The reason for this is easily seen. Zinc protects by galvanic action at the expense of being itself corroded. (It should be noted that the relative size of the surfaces of the two metals is a factor of tremendous importance in determining the extent of the corrosion or protection of one metal by contact with another.) In No. 19 the surface is zinc, with here and there a pin-hole exposing a minute bit of iron. The corrosion of zinc necessary to protect these microscopic surfaces of iron is so small in amount, and is applied to so large a surface of zinc, that a deposit of the

latter only 0.0002 in. (0.005 mm.) thick can protect the iron for months, if not for years, against ordinary atmospheric corrosion. In No. 20 such a deposit of zinc has been copper plated, with here and there a pin-hole through which the zinc is exposed. (The iron may or may not be exposed—the results as regards rusting will be the same.) Each pin-point of exposed zinc plate is surrounded by a relatively enormous surface of copper cathode, and in its endeavor to protect the copper against corrosion and tarnish the zinc is soon entirely dissolved, exposing the iron beneath it. This, like the zinc, acts as anode toward copper, and rusting is the result. Such a sub-coating of zinc can at best only slightly delay the rusting of iron plated with brass, copper, nickel, etc. If this practice is to be followed the zinc deposit should be made as thick as possible, in order to lengthen its life when once it is exposed and begins to act as anode. What is needed is a non-porous coating of nickel, brass or copper. Whether or not this can be obtained without going to the extreme thickness found necessary in these experiments is for someone of wider experience than the writer to say.

POROSITY OF ELECTRO-DEPOSITS.

The prompt rusting of the iron beneath the thinner deposits of all the metals except zinc seemed to indicate either that such deposits are porous in structure, or that there are small holes at certain points which leave the iron exposed. To study this question use was made of an ingenious, yet simple, method employed by W. H. Walker for detecting holes in tin plate.

A one and a half percent solution of agar was prepared, and to each hundred cubic centimeters of this 7 c.c. of a one percent solution of potassium ferrocyanide was added. The samples of plated iron were placed in a shallow glass dish and covered with the hot solution, which quickly set to a stiff jelly. In a short time numerous blue spots appeared on the thinner deposits.

With copper-plated iron the action is as follows: whenever there is a crack or hole in the plating a galvanic cell is formed in which the exposed iron is anode, goes into solution in the ferrous state, and is precipitated as Turnbull's blue, just as when a solution of potassium ferrocyanide is added to the solution of a ferrous salt in a test tube.

The results of this test are shown in Table XI. As these deposits were not weighed their thickness can only be estimated by a comparison of the ampere hours per square decimeter with those of Tables I, II, and IV.

TABLE XI.

Ferroxyl Test for Porosity.

Deposit	Time, min.	Temp.	Amp./dm.^{2}	Amp. Hrs./dm.^{2}	Blue-spots
Copper	1	Hot	5.5	0.09	Several
Copper	3	Hot	4.8	0.24	Few
Copper	5	Hot	5.6	0.47	None
Copper	10	Hot	5.6	0.94	None
Copper	20	Hot	5.9	1.99	None
Copper	40	Hot	5.9	3.91	None
Nickel	3	Hot	5.0	0.25	Many
Nickel	5	Hot	5.0	0.41	Many
Nickel	10	Hot	5.3	0.90	Many
Nickel	20	Hot	5.4	1.81	None
Nickel	40	Hot	5.1	3.4	None
Brass	3	Hot	11.1	0.55	None
Brass	5	Hot	10.4	0.87	None
Brass	10	Hot	11.8	1.96	None
Brass	20	Hot	11.8	3.93	None
Brass	40	Hot	11.3	5.65	None

All of the deposits were found to contain pin-holes with the exception of the brasses, but unfortunately no deposits of brass less than 0.55 ampere hours per square decimeter were prepared for this test. Copper coatings up to 0.47 and nickel up to 1.81 ampere hours per square decimeter contained pin-holes, but thicker deposits were free from them.

The remarkable protection afforded by very thin deposits of zinc must be due entirely to galvanic action, unless zinc coatings are free from the holes which have been shown to exist in thin deposits of all other metals tried in these experiments. The ferrocyanide test cannot be applied to zinc coatings however, since any exposed iron would be cathode, therefore would not dissolve, and so would not make its presence known by the blue precipitate. A test for the detection of pin-holes in electro-galvanizing, for which we are also indebted to Prof. Walker, consists in immersing the strips of galvanized iron in a hot, strong solution of sodium hydroxide; wherever a bit of iron is exposed it becomes the cathode of a voltaic cell, and hydrogen is evolved from it. The results of these tests are given in Table XII.

TABLE XII.

Porosity of Zinc Deposits by Sodium Hydroxide.

Deposit	Time Min.	Temp.	Amp./dm.²	Amp.Hrs./dm.²	Bubbles showing porosity
Zinc	1	Cold	12.1	0.20	Many
Zinc	3	Cold	16.6	0.83	Many
Zinc	5	Cold	11.8	0.98	Few
Zinc	10	Cold	9.1	1.52	None
Zinc	20	Cold	10.0	3.33	None

Thin zinc deposits proved to be as full of holes as were the coatings of other metals, and the freedom from rusting of lightly electro-galvanized iron is due solely to galvanic action. Deposits thicker than 1.5 ampere hours per square decimeter (14 amp. hrs. / ft.²) were free from holes.

PIN-HOLES BY INSPECTION.

Another method of testing for porosity consisted in examining the electro-deposits by transmitted light. To secure zinc deposits advantage was taken of the poor adhesion of electroplating on aluminum. Sheets of aluminum were polished, immersed for a few seconds in the electric cleaner, rinsed, and plated with zinc. The edges of the sheet were then cut away, and the deposit was stripped off and examined. The results are given in Table XIII.

TABLE XIII.

Porosity of Zinc Deposited on Aluminum.

Time, min.	Temp.	Amp./dm.²	Amp. Hrs./dm.²	Holes
5	Cold	6.32	0.52	Many
10	Cold	6.57	1.09	Few
20	Cold	5.55	1.85	None
30	Cold	5.12	2.56	None

At and above 1.8 ampere hours per square decimeter no holes were found—a good agreement with the previous test.

The lack of adhesion of electroplating on aluminum is due, in part at least, to an invisible film of oxide on the surface of the metal, and in spite of the good agreement seen in the last two sets of tests, there remained a suspicion that this film of oxide might cause electroplating on aluminum to be less uniform than on other metals. It was therefore decided to avoid the use of aluminum for receiving the deposit, wherever possible. Nickel, copper, and brass deposits were obtained by plating on zinc, and dissolving this in dilute sulphuric acid. A description of the deposits and the results of inspection are shown in Table XIV.

TABLE XIV.

Porosity of Metal Deposits on Zinc.

Deposit	Time, min.	Temp.	Amp./dm.^{2}	Amp. Hrs./dm.^{2}	Holes
Copper	3	Hot	8.2	0.41	Few
Copper	6	Hot	6.1	0.61	None
Copper	6	Hot	6.8	1.14	Few
Copper	10	Hot	7.5	1.20	None
Copper	20	Hot	6.5	2.18	Few—6 per square inch
Copper	40	Hot	7.8	3.12	Few—4 per square inch
Brass	3	Hot	12.0	0.60	None
Brass	5	Hot	12.0	1.0	None
Brass	10	Hot	12.0	2.0	None
Brass	20	Hot	12.0	4.0	None
Nickel	3	Hot	9.2	0.46	Many
Nickel	5	Hot	9.5	0.79	Many
Nickel	10	Hot	9.0	1.50	Several
Nickel	20	Hot	12.9	4.30	None
Nickel	40	Hot	12.9	8.60	None

This study of the porosity of electroplating seems to show that brass (0.000154 in. (0.0039 mm.) thick) and copper (0.000347 in. (0.0087 mm.) thick) deposits from the cyanide solution up to 0.5 ampere hours per square decimeter (4.6 amp. hrs. / ft.^{2}) contain pin-holes, and that nickel plating requires 1.5 ampere hours per square decimeter (14 amp. hrs. / ft.^{2}, 0.00102 in. thick) before pin-holes disappear.

In weathering tests of two to four months duration, rusting occurred on brass and copper plate many times thicker than the minimum for the disappearance of pin-holes. In case of the heavier deposits rusting was confined to spots a millimeter or less in diameter, the spaces between spots giving perfect protection to the iron beneath. For nickel plate there was good agreement between the disappearance of holes and freedom from rust. The divergence shown in this respect by copper and brass plating may possibly be due to the greater difference of potential between these metals and iron than that which exists between nickel and iron. The greater the difference of potential or corrosive force, the more difficult will it be to prevent rusting. For copper deposits there were no holes at 4.4 ampere hours per square foot (0.000347 in., 0.0087 mm., thick) and no rusting at 60.4 ampere hours per square foot (0.00248 in., 0.062 mm., thick). Similar values for brass plate are 5.1 amp. hrs. / ft.^{2} (0.000154 in., 0.0039 mm.) for no holes, and 20 amp. hrs. / ft.^{2} (0.00607 in., 0.152 mm.) for no

rusting. Nickel required 16.8 amp. hrs. / ft.^{2} (0.00108 in., 0.027 mm.) for the absence of holes, and 25.4 amp. hrs. / ft.^{2} (0.00146 in., 0.037 mm.) for freedom from rust.

The only hope of a general use of copper and brass plate on iron exposed to the weather seems to lie in securing a uniform deposit, free from pin-holes. In special cases it may be feasible to employ the extremely thick deposits of these metals which have been shown to be necessary to protect iron from the weather, but unless the plated article is fairly rigid there is danger of cracking and peeling of such heavy deposits, and the time and expense of producing them will prevent their general employment.

CONCLUSIONS.

1. These experiments confirm the orthodox view that the superiority of electro-galvanizing over deposits of other metals for the protection of iron is due to voltaic action.

2. It has been shown that thin electro-deposits of zinc, copper, nickel and brass are full of holes, and therefore only the first may be relied on to prevent rusting, unless deposits are made much heavier than is at present the rule.

3. Deposits of nickel should exceed 0.0015 in. (0.038 mm.) in thickness in order to protect iron out of doors, and copper or brass plate should have three times this thickness. Even then it is a question how long such coatings will afford protection.

4. For the protection by electroplating of iron which is to be exposed to the weather, zinc (or cadmium) is the only metal worthy of consideration.

5. The foregoing experiments do not show that double coatings—zinc followed by copper or brass—are distinctly superior to a single heavy coating of the latter metals. If zinc is to be used advantageously, it should form the outer coating.

6. It is very desirable that some method be found for producing a uniform electroplate, free from the holes which were responsible for rusting in these experiments. Could such plating be done deposits of nickel, copper and brass would form a far more effective protection to iron than at present.

Laboratory of Applied Electrochemistry,
University of Wisconsin.

DISCUSSION.

G. B. Hogaboom: The findings of Messrs. Watts and De Verter as given in their paper, with reference to double plating of zinc, and then either brass, nickel or copper, are in accordance with what we experienced about three years ago.

A door-check that was plated in a sulphate of zinc solution has been out, to my knowledge, three years, exposed at the side of a railroad track to the smoke of freight engines and it does not show a particle of rust, while some steel escutcheons that were given the same coating of zinc, and then given a coating of nickel, or of copper, or of brass, had in about one hundred and twenty days spots of rust. As soon as one spot developed then a greater number of them appeared quite rapidly. Why that happens is explained by Dr. Watts. According to his idea it is because one metal is electro-positive to the other and protects it. It is of vital importance to the hardware manufacturers to find some way of plating steel with a protective coating; brass, copper and nickel do not stand up under the usual atmospheric conditions very long.

Carl Hering: The paper refers frequently to pin-holes. Some years ago I read a paper before this Society describing experiments made with a microscope showing that suspended foreign particles in an electrolyte, like the dust from the room, traveled from anode to cathode, or the reverse, just like the ions do. It is not known what causes them to travel, but they do. Some of them will ultimately deposit on the cathode, and I am inclined to believe that is one of the causes of pin-holes. If, therefore, the solution around the cathode were kept perfectly free from suspended impurities, say by means of a diaphragm, there would be less likelihood of forming pin-holes.

Another thing which occurred to me in reading this paper was that the authors cleaned the iron by the ordinary pickling process. If they had cleaned it by electrolytic pickling, they would no doubt have gotten less pin-holes. If you examine iron under the microscope, iron that has been heated, like plates or castings, you will always find little specks of black oxide in the bottom of little depressions. In the ordinary pickling process many of these little specks do not come out. By looking at it afterward under a glass

one will still find these little black specks in these depressions. By the electrolytic pickling all of these specks can be dissolved, as the action gets down into the bottom of the deepest pits and without any useless waste of good metal and acid, as the pure metal is not dissolved. If more care were taken, I think the plating of iron would be more successful.

G. B. Hogaboom: In regard to the pin-holes, I do not think Mr. Hering's point is well taken for the reason that pin-holes will occur in the deposit of metal, even if there is a diaphragm. One of the hardest things to do in electro-plating is to deposit brass, copper or nickel upon electro-plated zinc without blistering, and these pin-holes seem to be the result of that. Better results can be had by sand blasting the surface, the zinc will adhere better, and even with that precaution little pin-holes will often form after it is plated with the brass or copper, while under the microscope the plate will not show any holes whatever. There is something in the action, in the nature of electrolysis, that causes the plate to blister.

Carl Hering: The particles I referred to are smaller than would be held back by your diaphragm. The only way they could be kept off would be by some diaphragm of organic material, or a porous cup, but not by means of any screen or bag, as they would go right through that.

J. W. Richards: I find in the conclusions a recommendation that the thickness of the plating should be a certain minimum thickness in order to afford complete protection. I think that the thickness of the plating necessary to give complete protection depends considerably on the original roughness of the surface, since a roughened surface commences to plate on the high points, and it takes some time for the plate to grow smooth and the plating to become continuous.

Other things being equal, the smoother the object the more quickly it will be coated continuously, and the rougher the object the longer it will take and the heavier the deposit to make a continuous coating.

G. B. Hogaboom: On a smooth article it is more difficult to make the nickel plate adhere than on a roughened object. For

successful plating, it seems to me to be necessary to have a slightly roughened surface, that is, a surface in an active state.

A. S. Cushman: It is not only in electro-plating operations one finds pin-holes. As a manufacturer of tin plate and terne plate, I do not think I have seen a fair-sized sample made by the hot-dip process that was free from pin-holes. It seems difficult to prepare the surfaces of iron and steel by any process whatsoever, to such a degree of excellence that other metals, either by electro-plating or hot-dip process, will cover them all up, and I think unless you do put on a heavy enough coating in order to build up on top of the pin-holes you could not get them filled up.

L. E. Saunders: My attention was called today to the fact that on some of the shells which are being manufactured in this country for the European nations that plating is required. Has any one any facts to give on that point? I understand that the Russian Government requires that steel shells must be coated with some other material to prevent rusting. Do you know anything about that, Mr. Hogaboom?

G. B. Hogaboom: I have had no experience with shells, but know that the finish depends upon the structure of the metal. Pin-holes will show if the metal has been overheated in the manufacturing process.

J. W. Richards: These pin-holes appearing in the metals which are heated differently, appear to be due to irregularities in the surfaces which are caused by the heat treatment. These cause irregularities in the deposition, because of the different conductivity of the cleaned surfaces and of the coated surface, or spots, caused by the heat treatment.

G. B. Hogaboom: I have seen deposits of silver which under a microscope showed the outlines of the structure of the steel upon which it was plated. The structure of the metal very materially affects the character of the deposit.

O. P. Watts (*Communicated* 23 Nov., 1916): In the five months which have elapsed since this paper was written rust has appeared on only one of the specimens previously reported in perfect condition, viz., on No. 32 six spots of rust show through the nickel plating.

A paper presented at the Thirtieth General Meeting of the American Electrochemical Society, held in New York City, September 28, 1916, Mr. L. E. Saunders in the Chair.

PRELIMINARY STUDIES IN THE DEPOSITION OF COPPER IN ELECTROTYPING BATHS.*

By W. Blum, H. D. Holler and H. S. Rawdon.

I. INTRODUCTION.

This work was initiated at the request of the Government Printing Office, and was conducted in co-operation with the International Association of Electrotypers.

Since the primary purpose of this research was the definition of conditions for the production of satisfactory electrotypes, the range of the experiments was more limited than would be desirable in a general investigation of copper deposition.

The Bureau has not yet completed its investigations on many of the phases of the subject discussed, and therefore wishes it clearly understood that the conclusions and recommendations are tentative only. The work is being continued and full details of methods of testing and of the results obtained, with a discussion of the literature on the subject, will later be published as a technologic paper of the Bureau, which will be announced in the technical journals when available. Directions for the operation of the electrotyping baths may be found in Circular No. 52, second edition, already issued by the Bureau.

II. METHOD OF PREPARING COPPER DEPOSITS.

The copper deposits were prepared at the Royal Electrotype Company of Philadelphia under commercial, but defined, conditions. The procedure used was as follows, being essentially the same as is used in practical work. One type form, selected so as to include type, rule, and half-tone work, and a considerable plain surface, was used throughout the tests. The wax molds were prepared from it under a suitable pressure and were coated

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with graphite by the wet process. They were then suspended in the copper solution contained in a new stoneware tank (with a capacity of 380 liters or 100 gallons) installed for this investigation. The solution was agitated by compressed air, and its temperature was regulated by circulating hot or cold water through a lead pipe immersed in it. The voltage was approximately adjusted by means of the field rheostat on the dynamo, and more accurately regulated by a carbon rheostat in series with the tank. Deposition was continued in each case till an average thickness (on the plain surface) of 0.2 mm. (0.008 inch) was secured, as calculated from the current density employed. The copper "shells" were then removed from the wax molds by means of hot water, and washed with hot alkali solution to remove adhering wax. They were then rinsed and dried, and sent to the Bureau of Standards for examination and test.

The following conditions were selected for the reasons given:

1. *Composition of Solution.* In all, seven solutions were used, in which the content of copper sulphate varied from 150 to 250 grams per liter, and of sulphuric acid from 30 to 100 grams per liter. This practically covers the working range, since the addition of sulphuric acid causes a marked decrease in the solubility of copper sulphate. The composition was determined by the methods described in Bureau of Standards Circular 52. No experiments were conducted with addition agents.

2. *Temperature of the Solution.* Experiments were conducted at 25° C. and 40° C. (77° F. and 104° F.) The former is the minimum practicable temperature at which the solution can be maintained during the passage of high currents; while the latter is the maximum that can be safely used with wax molds. It was impossible to maintain the temperature constant to better than about 3° C. in long runs. The effects of temperature over the range employed, were, however, so great that this uncertainty in temperature does not affect the practical conclusions.

3. *Agitation.* The solutions were given the highest practicable degree of agitation that could be secured by means of compressed air. Agitation by mechanical stirrers has not proven satisfactory for such baths.

4. *Current Density.* For each solution and temperature eight

deposits were made with current densities ranging from 2 to 10 amperes per square decimeter (about 20 to 95 amperes per square foot). This was accomplished by proper adjustment of the voltage and distance between anode and cathode as shown in Table I.

TABLE I.

Current Densities and Distances Employed.

		Run 1				Run 2			
Distance	cm.	15	10	7.5	6	15	10	7.5	6
	in.	6	4	3	2.4	6	4	3	2.4
Current Density	amp./dm.^{2}	2	3	4	5	4	6	8	10
	amp./sq. ft.	18	28	37	47	37	56	74	93

For each run the voltage was adjusted to secure the desired current densities by using approximately twice the voltage on Run 2 that was used on Run 1. The actual current density was measured for each deposit by means of shunts and a millivoltmeter.

III. METHODS OF TESTING COPPER DEPOSITS.

1. *Tensile Strength and Elongation.* Rectangular strips (120 x 15 mm.) were cut from the smooth portion of the copper deposits, two transversely and two longitudinally, *i. e.,* horizontally and vertically with respect to the position during deposition. The average thickness of each of these test specimens was computed from its weight and the density of copper (8.9). The specimens were tested in a Schopper machine, such as is used for testing thin sheet material. The ultimate tensile strength was calculated from the load required to break a specimen of measured cross section. The elongation was determined by measuring the distance after fracture between two gage marks (originally 5 cm. or 2 in. apart) placed upon the strip before testing.

2. *Hardness.* Thus far no satisfactory method of testing the hardness of such thin sheets of copper has been found. Experiments are now being conducted to determine whether the hardness as measured by the resistance to abrasion or to impact, is a criterion of the wearing qualities of the copper on a press.

3. *Microstructure.* Cross sections of the copper deposits for

examination of the crystalline structure were prepared by the methods ordinarily used in metallographic work. Certain precautions and modifications, however, were necessary. In order to polish cross sections of such thin specimens as these, they must be embedded in a suitable matrix, and the section taken through both the embedding material and the enclosed samples. Common solder was used as the matrix. The polished sections were etched with ammonium hydroxide and hydrogen peroxide to reveal the structure. The examination of the etched surfaces was made at a magnification of 300 diameters by reflected light (vertical illumination). In order to determine whether the heat of the molten solder used for embedding the other samples produced any change in the microstructure, several samples were prepared for microscopic examination by firmly clamping the copper specimens between two lead plates during the polishing. No such change could be detected by the microscope.

4. *Effect of Annealing.* For demonstrating the effect of annealing at relatively low temperatures upon the physical properties, three series of specimens of the size used for the tension test were held for periods of from 15 to 120 minutes at approximately 170°, 275° and 380° C. (338°, 527° and 716° F.) in a small electrically heated tube furnace. For temperatures of 275° C. and above, a gentle current of carbon dioxide was passed through the furnace to prevent oxidation of the samples, which could have caused a reduction of the cross section of the copper in the tension specimen.

Inasmuch as the annealing temperatures and periods given above did not produce any definite changes in the microstructure (though the tensile properties were changed) several samples of the copper deposited under widely varying conditions were annealed at approximately 610° C. (1,130° F.) for nearly two hours. No measurements of the physical properties were made upon these specimens, since such a temperature is far beyond anything reached in electrotyping practice.

IV. RESULTS OF TESTS.

1. *Tensile Strength and Elongation.* Tables and curves showing in detail the results of the numerous tests of tensile strength

and elongation will be included in the technologic paper. Owing to the difficulties involved in the testing of such thin material, the curves are not sufficiently regular to permit strictly quantitative conclusions to be drawn. It is believed, however, that the general conclusions given on page 64 are fully justified by the results obtained.

The results for ductility, as measured by the permanent elongation after fracture, were not sufficiently concordant or consistent to warrant graphic representation. In general the ductility increased with the tensile strength up to a tensile strength of about

FIG. 1.

Typical Coarse Structure. Deposited at 40° C. (104° F.) from a solution containing 200 g./L. (27 oz./gal.) of copper sulphate and 100 g./L. (13.4 oz./gal. of sulphuric acid, at a current density of 4.1 amp./dm.^{2} (38 amp./sq ft.). This specimen showed a tensile strength of only 1,560 kg./cm.^{2} (22,000 lb./sq. in.) and an elongation of only 11 percent. Magnification × 300.

2,800 kg./cm.^{2} (40,000 lb./sq. in.). Copper of greater tensile strength was frequently brittle. Since, however, only a few specimens obtained in this investigation had a tensile strength above 2,800 kg./cm.^{2} (40,000 lb./sq. in.), no sweeping conclusion is justified.[1]

In the various experiments the structure varied through a whole range of which three striking types are shown in Figs. 1 to 3.

[1] In this connection it is interesting to note that a few specimens of copper deposited from commercial baths said to contain organic addition agents, were found to have a tensile strength of over 3,500 kg./cm.^{2} (50,000 lb./sq. in.) with, however, an elongation of less than 5 percent.

FIG. 2.

Typical Columnar Structure (with occasional twinning) as in Fig. 1. Deposited at 25° C. (77° F.) from the same solution as in Fig. 1, at a current density of 5.3 amp./dm.^{2} (50 amp./sq. ft.). This specimen showed a tensile strength of 2,840 kg./cm.^{2} (41,000 lb./sq. in.) and an elongation of 30 percent. Magnification × 300.

FIG. 3.

Typical broken structure with frequent twinning. Deposited at 25° C. (77° F.) from the same solution as used in Fig. 1 at a current density of 6.8 amp./dm.^{2} (63 amp./sq. ft.). This specimen showed a tensile strength of 3,000 kg./cm.^{2} (42,500 lb./sq. in.) and an elongation of 27 percent. Magnification × 300.

The effects upon the physical properties of annealing ten samples taken from the same deposit are shown in Table II.

TABLE II.

Effect of Annealing Copper Deposit.

	Temperature		Time (min.)	Tensile Strength		Elongation
	0° C.	0° F.		(Kg./cm.²)	(lb./sq. in.)	
Unannealed	...	...	...	2840	41,000	30%
1	170	338	30	2740	39,000	20
2	170	338	60	2710	38,600	18
3	170	338	120	2740	39,000	17
4	275	527	30	2600	37,000	21
5	275	527	60	2590	36,900	24
6	275	527	120	2440	35,700	18
7	380	716	15	2250	32,000	29
8	380	716	30	2260	32,200	35
9	380	716	60	2260	32,200	36
10	380	716	120	2330	33,200	28

The effect upon the structure of annealing this same sample of copper at still higher temperatures is shown in Figs. 4 and 5.

V. CONCLUSIONS.

1. *Structure of Deposits.*

With low current density, especially at higher temperature, the copper possesses a relatively coarse structure except at the surface where the initial deposit is made. (Fig. 1.) By increasing the current density, particularly at lower temperatures, the structure assumes a columnar appearance, the crystals being long and finger-like (Fig. 2). With still further increase in current density, the crystalline structure is much broken up and numerous evidences of the twinning of crystals are found (Fig. 3). In every case the direction of growth of the crystals is perpendicular to the surface of deposition (see especially Fig. 6).

Twinning is of importance as indicative of the physical properties of the copper shell as a whole. Twinned crystals are usually found in material which has been annealed after distortion or cold working of some kind. This occurrence in the deposits as

laid down suggests strongly that the metal is in a condition of very high internal stress. If such is the case, the metal upon annealing should show a complete recrystallization. Fig. 5, which shows the same material as Fig. 2 after annealing, demonstrates that this assumption is correct. Coarsely crystalline deposits do not behave so upon annealing, indicating that the copper deposited at a slow rate is free from such internal stress, except at the surface of initial deposit, where the structure is very fine.

It is well known that any metal which is internally stressed by cold working (hammering, rolling, etc.) or from any other cause whatever, has physical properties very much different from those of the material not in such a condition. In general, material in a stressed condition has a much higher tensile strength than in the unstressed condition. It is to be concluded, therefore, that the properties of such deposits as these are not to be explained simply by the variations in crystal size or shape, but that due consideration must be given to the condition of the material in respect to internal stresses resulting from the conditions of deposition. In general, however, it may be stated that the finer the crystals, the higher is the tensile strength.

2. *Effect of Conditions upon the Tensile Properties.*

A. Agitation. With low current densities the degree of agitation does not have a marked effect upon the properties of the copper, while with higher current densities very efficient agitation is required to produce even coherent deposits. All the conclusions here given apply only to baths in which a high degree of agitation is employed.

B. Composition of Solutions. (*a*) Under otherwise uniform conditions an increase in the content of copper sulphate usually causes a slight increase in the tensile strength. (*b*) Under otherwise uniform conditions, an increase in the content of sulphuric acid at low temperature (25° C. or 77° F.) usually causes an increase in tensile strength, and at high temperature (40° C. or 104° F.) usually causes a decrease in tensile strength. These effects are most marked at intermediate current densities. No explanation for this anomaly is suggested. Further experiments at other temperatures are desirable to throw light upon this behavior.

FIG. 4.

Typical structure of annealed coarse deposit (before annealing the same as Fig. 1). Specimen annealed at 610° C. (1,130° F.) for 2 hours. Note that the only appreciable change in structure is at the surface of initial depostion. Magnification × 350.

FIG. 5.

Typical structure of annealed columnar deposit (before annealing the same as Fig. 2). Specimen annealed at 610° C. (1,130° F.) for two hours. Magnification × 300.

C. Temperature. A rise in temperature (from 25° to 40° C. or 77° to 104° F.) generally decreases the tensile strength. This effect is most marked with high acid content and with medium current density, in which case the decrease in tensile strength may amount to 50 percent.

D. Current Density. At low temperature, the tensile strength increases with increased current density, up to about 6-7 amp./dm.^{2} (56 to 65 amp./sq. ft.) and then remains nearly constant, or in some cases decreases slightly. At high temperature the tensile strength appears to pass through a minimum value which is reached at about 4 to 8 amp./dm.^{2} (37 to 74 amp./sq. ft.).

FIG. 6.

Distribution and structure of copper on the edge of a "rule" (*i. e.*, a line on the printed surface). Note that at the apex the copper is only about 30 percent as thick as at the base. Also that the direction of crystal growth is perpendicular to the surface of deposition. Magnification × 150.

3. *Thickness and Distribution of the Copper.*

At first it was assumed that upon a plane cathode surface parallel to the anode the copper would be deposited to nearly a uniform thickness. It was, however, found that differences of as much as 30 percent in thickness existed over even a small

portion of such a surface. In general the copper was found to be thickest near the bottom and outer edge, obviously owing to greater current densities at these points. The average thickness of the plain portion was from 80 to 90 percent of that calculated from the time and current used. There is always a considerable amount of copper deposited on the rough edges, thus accounting for the lower thickness in the center.

The distribution of the copper upon the rough type surface was very irregular. (See Figs. 6 and 7.) In general, as was to be expected, the copper was thinnest upon the printing surface, *i. e.*,

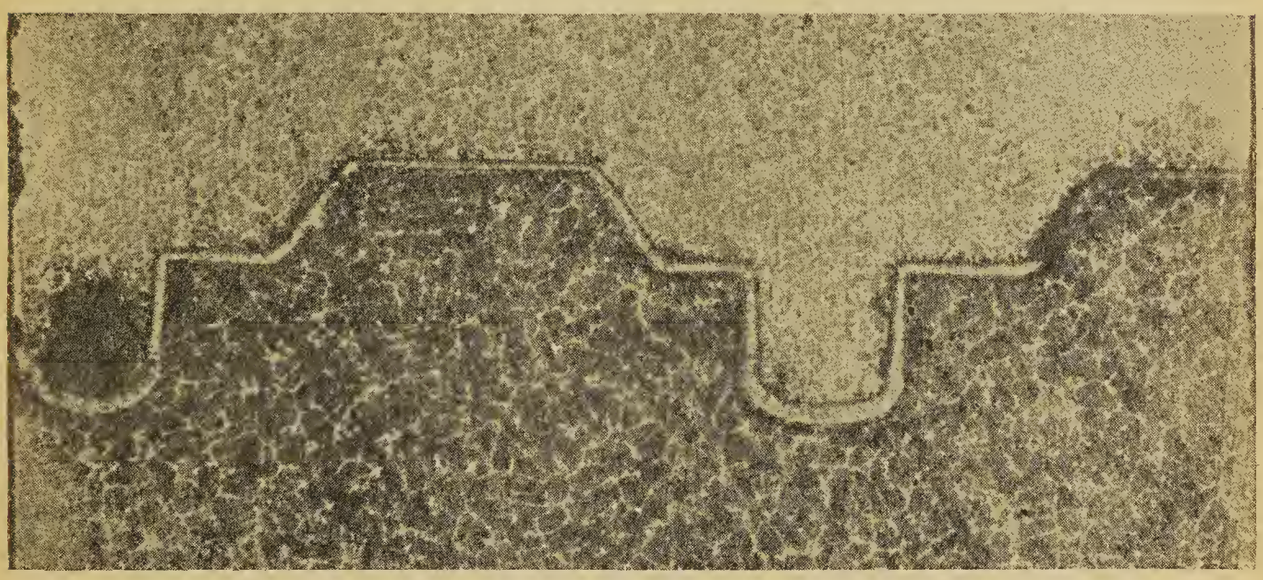


FIG. 7.
Distribution of copper on a type surface (embedded in solder). The light band represents the copper shell between the dark type metal below and the light solder above. The upper edge represents the printing surface. Magnification × 15.

the bottom of the depressions in the wax molds. The actual thickness of the copper upon different portions of the letters was only 30 to 50 percent of that calculated. Experiments showed that approximately the same weight of copper is deposited upon a given area (measured by its projection on a plane perpendicular to the direction of the current flow) whether the surface is plain, half-tone, or type; although in the latter case the actual surface of deposition is much greater than in the former. The observation is chiefly of interest in illustrating the impossibility of depositing a uniform thickness, or of computing the thickness of copper upon so irregular a surface. No definite effect of the distance between the electrodes (from 6 to 15 cm. or 2.4 to 6

inches) upon the structure of distribution of the copper could be detected.

4. *Effects of Annealing.*

The few experiments conducted upon the effects of annealing the copper (Table II) show that a decided decrease in tensile strength is produced by heating these thin specimens to temperatures of from 170° to 380° C. (340° to 720° F.), and that the greater part of this change occurs in the first 30 minutes. Annealing at the lowest temperature appears to cause a reduction in ductility, while at the highest temperature, the ductility was slightly increased. It is interesting to note that no corresponding changes in structure in the annealed specimens could be detected (microscopically), indicating, as previously suggested, that the change in tensile properties was caused by the relieving of internal stresses. Annealing at higher temperatures is required to produce visible structural changes (see Fig. 4).

VI. RECOMMENDATIONS FOR ELECTROTYPING BATHS.

The following recommendations are presented as defining the commercially convenient conditions for obtaining satisfactory deposits:

1. *Conditions for Deposition.*

Although no extended service tests of electrotypes containing copper of known properties have been made, examination of satisfactory electrotypes, and conference with practical electrotypers has resulted in the following tentative specification for copper for electrotypes, viz., a tensile strength of 2,500 to 2,800 kg./cm.^{2} (35,000 to 40,000 lbs./sq. in.), and an elongation of 20 to 30 percent. For the production of such copper, the following conditions are recommended as being the most convenient for commercial practice.

A. Composition of solution. The solution should contain from 50 to 80 g./L. (7 to 11 oz./gal.) of sulphuric acid, and from 250 to 200 g./L. (34 to 27 oz./gal.) of copper sulphate. In other words, the total content of copper sulphate plus sulphuric acid should be about 300 g./L. (40 oz./gal.). This corresponds to a specific gravity of 1.18 (22° Baumé)[2].

[2] H. D. Holler and E. L. Peffer, Bur. of Stand. Sci. Paper No. 275; J. Am. Chem. Soc., 38, p. 1021; 1916.

B. The solution should be maintained between 25° and 30° C. (77° and 86° F.), unless high current densities are used. If the current density is above 8 amp./dm.^{2} (75 amp./sq. ft.), the temperature may be allowed to rise to 35° C. (95° F.).

C. Current density. At low temperature current densities from 5 to 9 amp./dm.^{2} (47 to 84 amp./sq. ft.) may be employed. At 35° C. ((95° F.) current densities from 8 to 10 amp./dm.^{2} (75 to 93 amp./sq. ft.) are most satisfactory.

D. Agitation. The highest practicable degree of agitation should be employed, especially between the anodes and cathodes.

2. *Annealing Effects.*

It is probable that during the process of "backing up" the shells with molten type metal, the copper of the shells is heated to such a temperature that some annealing takes place, similar to that described on page 162. The extent to which this occurs, or its effect upon the wearing properties of the plates, is difficult to determine. Examination of a number of finished electrotype plates, some prepared from copper deposited under known conditions, indicates that any such annealing effect has not been sufficient to make any visible change in the micro-structure, though it may have produced some change in the tensile properties, such as is shown in Table II.

VII. SUMMARY.

From a study of the tensile strength, ductility and microstructure of copper deposited from copper sulphate-sulphuric acid solutions, upon graphited wax molds, the effects of the various conditions of deposition upon the properties of the copper were determined. The convenient conditions for satisfactory operation of copper electrotyping baths have been described. The authors desire to express their appreciation to Messrs. E. L. Lasier and P. D. Sale, of this Bureau, for assisting in the tensile strength tests.

Bureau of Standards,
Washington, D. C.

DISCUSSION.

WILLIAM BLUM: Electrotyping, like electro-plating, has in the past been an empirical industry, the work being carried on without carefully testing the composition of the solutions. The object, in brief, of the present investigation was to determine the effect of the various factors upon the structure and properties of the copper, and from these conclusions to make recommendations regarding the best conditions of operation. In contrast to the needs of electro-platers, electrotypers are concerned not so much with the structure or possible appearance of the deposits as with their actual mechanical properties. In order to determine these we measured the tensile strength and elongation. Unfortunately, we have not yet been able to devise methods of testing satisfactorily the hardness, *i. e.*, the actual abrasion hardness, of these thin deposits. As you can understand, with deposits of metal as thin as these none of the ordinary methods of testing hardness are applicable. That is a part of the investigation which has not been completed, therefore to that extent this is a preliminary report of the work, although the main conclusions will probably not be greatly changed.

LEONARD WALDO: I think the Bureau of Standards is building better than it knows in offering such a contribution as this. I do not see in it the kilowatt-hour values of the deposit. I have not had any opportunity of reading the paper carefully, but the fact that the tensile strength, coherence, so to speak, of the deposit is a function of temperature and current density is an important thing.

I think we would be very glad if the Bureau of Standards would extend this deposition study to other metals than copper, paying particular attention to the relation of the amount of metal deposited per kilowatt-hour as a function of temperature and current density.

WILLIAM BLUM: That point has not been gone into in this particular work, for the reason, as pointed out by Mr. Hogaboom, that the question of either current or power efficiency is not a very vital one in such work, where the total cost of producing

the copper shell is only a very small part of producing the finished electrotype.

The point is, however, of interest and we expect to bring it out in a more complete publication which we hope to make, in which we will include the various voltages required for operating under these different conditions. From these, of course, it will be possible to calculate the efficiency, and the benefit derived from using, for example, a solution of better conductivity.

The circular of the Bureau of Standards No. 52 gives the main conclusions of this work, as well as general information, and conversion tables for electrotypers.

C. G. Fink: Would it be of any advantage to the electrotyper to use a wax of decidedly higher melting point than the wax he is using now?

William Blum: I do not believe that would be any great advantage, for the reason that the difficulties involved in regulating the temperature of the mold, taking the impression, etc., might be increased.

While this has no direct bearing on electro-deposition, we have, as a matter of fact, for the last several months had to interrupt our work on electro-deposition, and study the molding wax because the electrotypers cannot get ozocerite. We find that most electrotypers are taking impressions slightly above room temperatures, perhaps in the neighborhood of 40° C. On the other hand, they have at the present time no facilities for molding at higher temperatures. If they make deposition on lead molds, as is done for halftone work, the temperature is not important.

G. B. Hogaboom: At higher temperatures would not the wax have a tendency to break?

William Blum: That would depend on the properties of the particular wax.

F. C. Frary: Does Mr. Blum feel justified in drawing conclusions from experiments where the total variation between extremes of the tensile strength is only 10 percent or less, as in some of the specimens exhibited?

William Blum: I am glad you called attention to that. These specimens were taken at random from those at our exhibit. Some

of these specimens show that the effect of some factors was not very great. The total range in the tensile strength was, however, over 100 percent, *i. e.,* we obtained copper deposits having from 1400 to 2800 kilograms per square centimeter tensile strength. The only reason the curves were not given in the paper is because they were not so smooth as would be desirable, since there was one factor which we could not control or define accurately, *i. e.,* the agitation. The agitation of an electrotyping bath is produced by means of compressed air, and even though we took various measures to regulate the degree of agitation, we were unable to produce a strictly uniform agitation over the entire surface (about 9 sq. dm. or 1 sq. ft.) and at different times.

As previously stated the temperature effect was very great. On the other hand, this work was done in a commercial plant, where we could not regulate the temperatures closer than within 2° or 3° C.

W. S. Tyler: On page 163, Dr. Blum refers in a foot-note to the effect of the addition of organic substances, and he speaks of the high tensile strength with small elongation. I would say that some time ago I submitted a sample to the Bureau of Standards, and while at that time I was doubtful of the composition of the bath, I afterwards found that it did contain organic substances, and we got an elongation between 22.5 and 24 percent, with a tensile strength of 47,000 lb. per sq. in., or something over 3300 kilograms per square centimeter.

William Blum: I must state here that no investigation of the addition agents was made. A few tests were made upon samples of copper sent from people who we know are using addition agents. In general we found that such samples possessed a high tensile strength and a low elongation; but I would not wish to make the statement in the foot-note the basis of any general conclusion regarding the effect of addition agents.

A paper presented at the Thirtieth General Meeting of the American Electrochemical Society, held in New York City, September 28, 1916, Mr. L. E. Saunders in the Chair.

CONTRIBUTIONS TO THE KNOWLEDGE OF THE ELECTROLYSIS OF AQUEOUS SOLUTIONS OF VANADIUM SALTS.

By Siegfried Fischer, Jr.

INTRODUCTION—LITERATURE ON ELECTROLYTIC VANADIUM.

Previous to 1882, very little electrolytic work was done on vanadium, but since then much interest has developed in this field. Electrolytic processes may be divided into (1), those using an aqueous electrolyte, and (2), those using a non-aqueous or fused electrolyte. The electrolytic processes for obtaining metallic vanadium, using either aqueous or fused electrolytes, are very few, and most are of theoretical value only. The literature on the subject is very scant, and much of the data reported lacks accuracy.

It is the object of this thesis to determine whether or not it is possible to obtain metallic vanadium from aqueous solutions of its salts.

Electrolysis of Vanadium Electrolytes.

The literature on electrolytic processes for obtaining metallic vanadium is very scarce, but a considerable amount of work has been done by various scientists on the electrolytic behavior of vanadium compounds. The work is of importance, because in treating an ore or a vanadium product by electrolysis, the vanadium will always be in solution as a compound, which must be decomposed by the electric current. The literature may be conveniently divided into

1. General Literature on Electrolysis of Vanadium.

2. Electrolysis of Aqueous Solutions of Vanadium Salts for obtaining Metallic Vanadium.

1. *General Literature.* Der Zustand Einiger Übersaüren und ihrer Salze (the condition of some super acids and their salts in

solution), in the "Zeitschrift für physikalische Chem.," **43** (1903), 160-178. L. Pissarjewsky studied the conductivity, behavior and composition of the potassium salts of the acids HVO_4 and $H_8V_6O_{26}$, and found that these compounds are much too complex to yield metallic vanadium on electrolysis, but simply an oxide.

According to L. Marino—Über das elektromotorische Verhalten des Vanadins (about the electromotive behavior of vanadium), "Zeitschrift für anorganische Chemie," **39** (1904), 152-169, the lower oxides of vanadium behave like those of chromium, while its higher oxides resemble those of phosphorus and arsenic. If vanadium is used as an anode it acts as a reducing agent in solutions of neutral salts of silver, gold, platinum and iridium, reducing the salts to the metallic state, on connecting the anode and cathode leads, while $Cu^{\cdot\cdot}$, $Hg^{\cdot\cdot}$ and $Fe^{\cdot\cdot\cdot}$ ions are only partially reduced to $Cu^{\cdot}$, $Hg^{\cdot}$ and $Fe^{\cdot\cdot}$. Vanadium exerts no reducing action on $Zu^{\cdot\cdot}$, $Cd^{\cdot\cdot}$, $Ni^{\cdot\cdot}$ and $Pb^{\cdot\cdot}$. The vanadium enters the solution anodically as tetra-valent ions ($V^{\cdot\cdot\cdot\cdot}$). Marino has shown experimentally that, in an alkaline solution, vanadium enters solution as penta-valent ions ($V^{\cdot\cdot\cdot\cdot\cdot}$), while in an acid solution it dissolves as tetravalent ions ($V^{\cdot\cdot\cdot\cdot}$). The potential for the reaction $V \rightarrow V^{\cdot\cdot\cdot\cdot}$ was found to be approximately —0.3 to —0.4 volt. The article contains much experimental data, but unfortunately they lack accuracy, due to the experiments being conducted with vanadium which contained 8.66 percent carbon.

Muthmann and Frauenberger showed that vanadium under certain conditions possessed passivity. Pure vanadium in a normal solution of potassium hydroxide shows at the beginning a potential of —0.13 volt; but after ten minutes a maximum value was obtained, namely 0.737 volt. This property of passivity is shown more or less after treating the vanadium with oxidizing agents or after anodic polarization. ("Berichte der königlichen bayrischen Akadamie der Wissenschaften zu München.")

Under "Vanadium," in Abegg's "Handbuch der anorganischen Chemie," Vol. III, 683-788, is found valuable information regarding the behavior of the various vanadium ions. Tetravalent compounds may show either acid or basic properties. The acid compounds have formula VX_4, while the basic are of the type VOX_2. Under this latter type of ion comes the vanadyl-ion ($VO^{\cdot\cdot}$) and the divanadyl-ion $(V_2O_2)^{\cdot\cdot\cdot\cdot}$. The cathions ($V^{\cdot\cdot\cdot\cdot}$) or

$V(OH)^{\cdots}$ show weak electric but strong hydrolytic properties. The trivalent ion ($V^{\cdots}$) shows strong positive properties. It is different from the ions of the other metals of the same periodic group, as it does not form the compound VH_3. The electro-positive property of the tri-valent ($V^{\cdots}$) ion is not very great, because this ion very readily forms double salts, similar to $Al^{\cdots}$, $Fe^{\cdots}$, $Cr^{\cdots}$ and $Mo^{\cdots}$. The di-valent ion ($V^{\cdot\cdot}$) possesses still stronger positive character. It forms double salts with $FeSO_4$ and $MgSO_4$, strongly resembling the magnesium group of metals. The di-valent ion is very readily oxidized, and in its reducing power reminds one of the $Cr^{\cdot\cdot}$ ion.

In a dissertation entitled "Measurements of the reduction potential of solutions of diverse solutes forming vanadium compounds," published in Leipzig in 1906, T. F. Rutter gives the results on the determination of the electromotive behavior of the chains, $V^{\cdot\cdot} \rightarrow V^{\cdots}$, $V^{\cdots} \rightarrow V^{\cdots\cdot}$, and $V^{\cdots\cdot} \rightarrow V^{\cdots\cdots}$ from solutions containing V^{II} and V^{III}, V^{III} and V^{IV}, and V^{IV} and V^{V} compounds in changeable quantities. The solutions investigated were compared with a mercuro-sulphate electrode in a 0.5 normal H_2SO_4 solution of potential 0.679 volt. The results obtained are as follows:

$$V^{\cdot\cdot} \rightarrow V^{\cdots}$$

0.1n V^{II}; 0.5n H_2SO_4 (free from V^{III})	Potential	0.909	volts
0.05n V^{II}; 0.05n V^{III}; 0.5n H_2SO_4	"	0.889	"
0.033n V^{II}; 0.066n V^{III}; 0.5n H_2SO_4	"	0.881	"
0.025n V^{II}; 0.075 V^{III}; 0.5n H_2SO_4	"	0.875	"
0.1n V^{III}; 0.5n H_2SO_4 (free from V^{II})	"	0.464	"

(Mercury electrode used was positive.)

$$V^{\cdots} \rightarrow V^{\cdots\cdot}$$

0.1n V^{III} (free from V^{II} and V^{V})	Potential	0.462	volts
0.075n V^{III}; 0.025n V^{IV}	"	0.397	"
0.05n V^{III}; 0.05n V^{II}	"	0.373	"
0.025n V^{III}; 0.075n V^{II}	"	0.363	"
0.1n V^{IV} (free from V^{III} and V^{V})	"	0.051	"

(Mercury electrode used was positive.)

$$V^{\cdots\cdot} \rightarrow V^{\cdots\cdots}$$

0.1n V^{IV} (free from V^{III} and V^{IV})	Potential	0.051	volts

(Mercury electrode, used positively.)

0.05n V^{IV}; 0.05n V^{V}	Potential	0.241	volts
0.1n V^{V}; 0.5n H_2SO_4 (free from V^{IV})	"	0.462	"

(Last two experiments, mercury electrode used negatively.)

Rutter also found that vanadium of its own accord could form ions of the type $VO^{\cdot\cdot}$ from $V^{\cdot\cdot\cdot\cdot}$; VO_2'', VO_3', and V_6O_{17}''''. Also if the ratio of ($V^{II} \cdot V^{III} = 0.05 \cdot 0.05$) and ($V^{III} \cdot V^{IV} = 0.05 : 0.05$) existed, then the single potentials are respectively + 0.21 and — 0.30. This means that the tendency to form V^{II} to V^{III} is greater than the tendency to change H to $H^{\cdot}$, and the potential to change V^{III} to V^{IV} is greater than that to change Ag to $Ag^{\cdot}$: therefore, vanado-salts liberate hydrogen, and vanadi-salts liberate silver or copper of the solution of copper sulphate used is concentrated and heat applied. Vanadyl salts, according to the author are very weak reducing agents, they being readily oxidized by permanganic acid, chromic acid and hydrogen peroxide, slowly by persulphates, and only slightly by iodine and bromine. Rutter also established the fact that various oxides of vanadium immediately come to an equilibrium. Further information on this subject may be found in an article published by the same author in the "Zeitschrift für anorganische Chemie," **52**, 368-396, on "The Contribution to the Knowledge of the Compounds of Vanadium." This article deals in detail with the extract given from his thesis.

Stahler and Wirthwein prepared vanadic salts $(V)^{\cdot\cdot\cdot}$ and followed the progress of reduction by titrating part of the electrolyte at different stages of the experiments with potassium permanganate ("Berichte," **38**, 3978).

A. Bültemann quotes the work of Piccini and Brizzi who, in the "Zeitschrift für anorganische Chemie," **11**, 106, and **19**, 394, published two articles on the reduction of penta- and tetra-valent vanadium salts by means of electrolysis. Both articles show that the penta- and tetra-valent compounds are reduced to the tri- and di-valent state respectively, by electrolysis. Bültemann continued the investigation of the double salts of vanadium, corresponding to the ordinary alums. The preparation of these vanadium alums by electrolysis was based fundamentally on keeping the anode and cathode liquors separated by means of a porous cell. He describes the apparatus used and the various salts prepared. The only one of interest is the vanadium-ammonium alum, $V_2(SO_4)_3(NH_4)_2SO_4.24H_2O$. The anode liquor used was sulphuric acid of the same concentration as the cathode liquor, which consisted of 100 cubic centimeters of a sulphate solution

of tetra-valent vanadium. The catholyte was prepared as follows: 25 gm. of acid ammonium metavanadate was dissolved in 31.4 grams of concentrated sulphuric acid, and heated on a water bath with 200 cc. of saturated sulphurous acid until all the vanadium was in solution. This solution then had a blue color, indicating the presence of the tetra-valent compound. This process requires time, and much of the water was evaporated. After cooling, the solution was filtered; the filtrate after being made up to 100 cc. was ready for electrolysis. The anolyte was put into the porous cup and placed in a beaker of convenient size, and the catholyte added. A platinum wire, 0.15 cm. in diameter, served as anode. The cathode was circular in shape, having an area of 160 square centimeters, and was made of lead. Good circulation of the electrolyte was required which was accomplished by introducing a current of hydrogen. Used 8 amperes, that is 0.05 ampere per square centimeter. Duration of experiment was 43 minutes; voltage 8 to 9; temperature 80° C. At the end of the experiment, the catholyte was poured off and allowed to cool in a closed vessel. A large quantity of bluish-violet crystals of vanadium ammonium alum separate out.

Bültemann observed that this alum occurs in two modifications, analogous to chromium aluminium. By treating the ammonium metavanadate with less sulphuric acid than called for above, he obtained after electrolysis a brown solution instead of a green one, as before; and the crystals separating out were of garnet color instead of bluish-violet. These red crystals in acid solution changed to the bluish-violet crystals. The garnet crystals may also be obtained by recrystallizing the bluish-violet ones from an acid solution. The alum is fairly stable, but if the solution is in contact with air it readily oxidizes. ("Zeitschrift für Elektrochemie," **10**, 141-143. Contribution to the knowledge of the electrolytic preparation of tri-valent vanadium salts.) This alum may prove of value in obtaining metallic vanadium from aqueous electrolytes (Fischer).

Eugen Renschler prepared the tri-valent vanadium ammonium sulphate similarly to Bültemann, "Zeitschrift für Elektrochemie," **18**, 137 (1912). The preparation of vanadium salts by electrolysis.

Dr. R. Luther found that chloric acid oxidizes more readily by

electrolysis if tri-valent vanadium is present in the electrolyte. With no vanadium present in the acid solution 1.8 volts were required for electrolysis at the start, rapidly decreasing to 0.6 volt; with vanadium present the electromotive force rose to 2.2 volts. When the ClO_3 ion was present there was much less polarization. "Elektrochemische Aktivierungserscheinungen" (The electrochemical activity shown by vanadium compounds), "Zeitschrift für Elektrochemie," **13**, 1907.

Bleecker mentions a method for obtaining vanadic acid electrolytically. Notes on the chemistry and metallurgy of Vanadium: "Metallurgical and Chemical Engineering," **8**, 666-671; and **9**, 209-213, 499-505. The article is divided into three parts: I. The Chemistry; II. Methods of Analysis, and III. The Metallurgy. Sodium vanadate liquor, free from chlorides, is purified by making the solution slightly alkaline with sodium carbonate and heating up to 90° C. The liquor is decanted into an evaporator and concentrated to 30° Baumé, giving a solution which will contain about 200 gm. of vanadic acid per liter, depending upon the amount of sodium vanadate present. Electrolyze in a compartment cell, consisting of a porous cup of 8 liters capacity which contains the vanadium liquor, and a jar holding 5 to 10 gallons (19 to 39 liters), containing a dilute solution of sodium hydroxide. The anode is platinum foil 6 in. x 6 in. (15 cm. x 15 cm.), and the cathode is either iron or copper; preferably the latter. The voltage used depends upon the resistance of the porous cell and is about 6 to 8 volts. The current density will be 30 amperes per square foot (33 amp. per sq. dm.). The sodium ions pass through the porous partition into the cathode compartment, leaving vanadic oxide ions in the anode compartment. Since sodium vanadate is very soluble in water, and vanadic acid practically insoluble, a precipitation occurs on removing the alkali. The presence of mineral acids interferes seriously with the reaction, since vanadium oxide is soluble in dilute acids. If small amounts of chlorine are present in the electrolyte it is partly liberated at the anode, part forms complex vanadyl compounds, giving an impure product. The presence of sulphuric acid causes the precipitation of sodium vanadyl-sulphate containing 73 percent vanadic acid. Any lime or silica not previously removed by filtration will precipitate in part in the anode compartment just

as the solution becomes neutral. Some impurities enter the product in spite of the best care taken in the manipulation, probably due to the disintegration of the porous cell.

A patent was granted Bleecker on a process for the electrolytic separation of vanadium and uranium (U. S. Pat. 1,050,796, Jan. 21, 1913). The solution containing these two elements is heated to 90° C., and treated with sodium hydroxide in sufficient quantities to precipitate the uranium. The precipitate thus formed contains some vanadium hydroxide which is recovered by electrolysis as follows: the precipitate is well washed with water and then dissolved with sulphuric acid. The solution is then made slightly alkaline with sodium carbonate and electrolyzed with an anode of iron, nickel, or copper. The vanadium is recovered as vanadium oxide, an anode product, the uranium remaining in solution.

P. Truchot determined vanadium by electrolyzing a hot, slightly ammoniacal sodium vanadate solution. The solution was decomposed, depositing the vanadium as an oxyhydrate on the cathode. The vanadium content of the solution may be from 0.012 to 0.05 gm. vanadic acid per 200 cc. of electrolyte. Temperature of electrolyte, 80° to 90° C. The voltage employed was 2 to 2.25 volts, and the current density was 0.3 amperes per 8 square centimeter cathode surface. The electrolysis lasted 8 to 10 hours. The successful operation requires that the volume of the electrolyte be kept constant by the addition of water from time to time. The water added should contain a little ammonia. The oxyhydrate is precipitated on the cathode as a brown deposit, and when dried and heated gives vanadic acid. "Les Annales: Chimie analytique applique, **7**, 165-167." "Chemisches Zentralblatt," LXXIII, **5**, 1423-1424.

R. E. Myers electrolyzed a sodium vanadate solution acidulated with sulphuric acid, using a mercury cathode. The electrolyte changed from a blue to a green color, but no increase in weight was observed at the cathode. ("Electrochemical Analysis by use of a Mercury Cathode," Journal of the American Chemical Society, **26**, 1130.)

2. *Electrolysis of Aqueous Solutions of Vanadium Salts for Obtaining Metallic Vanadium.* In a statement made by Bleecker

in his article on the Chemistry and Metallurgy of Vanadium, in the Metallurgical and Chemical Engineering, **8**, 666-671, he declares that he has never found vanadium to possess electropositive properties, but that it is always found as an anode product. Truchot, however, claims to have found a cathode product in the form of an oxyhydrate. Sherard-Cowper-Coles, Setterberg and Fischer also obtained vanadium, or some vanadium compound, at the cathode.

In general, it may be said that nearly all of the attempts to obtain metallic vanadium from aqueous solutions by electrolysis have failed, with the exception of the method used by Cowper-Coles, and his work even is doubtful, as several investigators have not been able to repeat his experiments successfully.

L. Schicht in the Chemical News, **41**, 280; and **42**, 331, describes his work on electrolytic vanadium. It is, in brief: vanadium chloride was dissolved in water and hydrochloric acid, and this solution then electrolyzed. No deposition took place in the blue solution, the vanadium compound being merely reduced.

G. Gore, in his book on Electrochemistry, describes attempts to obtain metallic vanadium (pp. 101 to 102). 1. A solution composed of vanadic acid dissolved in pure dilute hydrofluoric acid was electrolyzed with a current obtained from ten Smee elements. Electrodes used were a gas carbon anode and a platinum cathode. A gas having the odor of ozone was liberated at the anode. No vanadium was obtained. 2. A dilute sulphuric acid solution saturated with ammonium vanadate was electrolyzed, using platinum electrodes; a current was supplied from four zinc and platinum elements excited by dilute sulphuric acid. The conductivity of the vanadium solution was very low. During the electrolysis the solution changed gradually to a very intense bluish-black color at the cathode, and a jet black powder of some thickness was deposited on it.

C. Setterberg did not obtain metallic vanadium on electrolyzing a solution containing a vanadium salt. On electrolyzing a solution of ammonium meta-vanadate he obtained a dark red precipitate of vanadic acid at the anode. Ammonia was liberated at the cathode. Furthermore, he subjected a concentrated solution of V_2O_4 dissolved in hydrochloric acid to electrolysis, using a porous cell. The blue solution in the porous cell became dark brown in

color very rapidly, and a black, brittle deposit was obtained on the cathode. The compound in all probability was the sesquioxide of vanadium. Vanadic acid was deposited on the anode. Solutions of vanadyl chloride and tetrachloride showed such low conductivity that they could not be used. (Gmelin and Kraut: "Handbuch für anorganische Chemie," Vol. III_2, p. 64.)

Sherard-Cowper-Coles claims to have succeeded in electrolytically depositing metallic vanadium as follows: The electrolyte was prepared by boiling vanadic acid with an excess of sodium hydroxide and decomposing the vanadate thus formed with an excess of hydrochloric acid. In detail: Dissolve 1.75 parts of vanadic acid (V_2O_5) and two parts of sodium hydroxide in 160 parts of water; to this clean solution add 32 parts of hydrochloric acid. The solution thus formed will contain one ounce of vanadic acid per gallon (106 gm. per liter). Current density used was 18 to 20 amperes per square foot (2.0 to 2.2 amp. per sq. dm.); the voltage was 1.88 volts between the terminals. The electrolysis was conducted at a temperature of 180° F. (82° C.). Experiments were performed, using a higher and a lower current density, but the results were unsatisfactory, as the metal at the cathode was contaminated with red oxide. It was found that the temperature also has an important rôle, as it causes an impure cathode product if it is below 180° F. (82° C.). Under the conditions described above, silvery metallic vanadium having very high metallic luster was deposited and adhered tightly to the cathode. The solution when first made is greenish-yellow in color. After boiling with a carbon anode it becomes darker, and on passing the current is changed to a dark green. When much metal was deposited out, the color changed to a bluish tint. When two ounces of vanadic acid per gallon (212 gm. per liter) were used, the deposited metal, instead of being a silvery white, was grayish in color. ("Institution of Mining and Metallurgy," 1898 and 1899, pp. 198 to 200; and "Chemical News," 1899, p. 147. "Notes on the Electrodeposition of Vanadium.")

Great hope was expressed, in the Spanish journal *Revista Minera,* in the development of the Cowper-Coles process, as Spain at that time had the richest known vanadium deposits; but the process never became commercial. ("Zeitschrift für Elektrochemie," **6**, 171, 1899 to 1900.) Borcher and McMillan claim

that they never succeeded in repeating Cowper-Coles' experiments. ("Electric Smelting and Refining," pp. 489 to 490.)

Gustav Gin states that, on repeating the work of Cowper-Coles, he observed that the metallic deposit soon stops, tarnishes and does not exceed a very limited thickness. According to Gin, it seems that the deposit is at first protected by a film of hydrogen, which soon loses its efficacy. Gin believes that at the present time (1909) it is impossible to produce metallic vanadium commercially from aqueous solutions by means of the electric current. (Trans. Amer. Electrochem. Soc., **16**, 439-441.)

The object of this thesis is to determine if it is possible to deposit metallic vanadium from aqueous salt solutions by means of the electric current This question has never been satisfactorily answered, and the amount of work done along this line does not permit of a definite conclusion.

In the introduction is given an outline of the work done up to date. The only reference found, which gives conditions whereby metallic vanadium was obtained is that of Sherard-Cowper-Coles: "Notes on the Electrodeposition of Vanadium," published in the "Institution of Mining and Metallurgy," 1898 and 1899, pp. 198 to 200. This, then, is the natural starting point and, while the electrolyte should come rather under the head of mixed salts, the investigation was undertaken for the purpose of improving the Cowper-Coles method, if possible, and making the process a commercial one.

Experimental Work.—Part I.

Investigation of Sherard Cowper-Coles' Work. In his treatise on the subject, Cowper-Coles gives the conditions under which he claimed to have obtained the metal. He also describes the deposit obtained. The electrolyte which he used consisted of 1.75 parts vanadic acid (V_2O_5); 2.00 parts sodium hydroxide, and 160.00 parts water. This mixture was then boiled, and 32 parts of hydrochloric acid added.

He studied various current densities and changes in temperature, and claimed the best results for the following conditions: 18 to 20 amperes per square foot (2.0 to 2.2 amp. per sq. dm.) cathode surface (0.125 to 0.139 amperes per square inch); voltage, 1.88 volts; temperature, 180° F. (82.2° C.). Under these

conditions it was claimed that the vanadium obtained was very dense and its color that of silver.

In order to get the proper conditions for depositing metallic vanadium, a series of 55 experiments was made, starting with the conditions given by Cowper-Coles; and then changes were made in current density, in temperature, in cathodes, and in concentration. The effect of addition agents was investigated, and the action of the electric current on the neutralized electrolyte of Cowper-Coles was studied. Tests also were made, using a porous partition to keep the catholyte and anolyte separated. The results are tabulated in Table I.

Summary and Conclusions.

1. Metallic vanadium cannot be obtained by electrolyzing the Cowper-Coles electrolyte.

2. The reduction of the electrolyte is limited in most cases to the vanadyl state, which is blue (V_2O_4).

3. With the exception of experiments 12 to 15, and 40 to 43, all tests show a reduction of the electrolyte.

4. With high temperatures (90° C. or over) the reduction can go to the V_2O_2 state, lavender color.

5. Lead electrodes alone give a reduction to the sesquioxide or green state (V_2O_3) at temperatures below 90° C. Above 90° C. the electrolyte is reduced to the lavender state (V_2O_2).

6. Carbon electrodes reduce the electrolyte to the sesquioxide form (V_2O_3), green color.

7. Platinum cathodes at temperatures below 90° C. reduce the electrolyte to the blue vanadyl state only (V_2O_4), and the current density seemingly has no further effect. At temperatures of 90° C. and above the lavender state (V_2O_2) is reached only when porous cells are used; otherwise not.

8. The black deposit on platinum cathodes is not a vanadium compound.

From these 55 experiments, it is clear that metallic vanadium cannot be obtained from Cowper-Coles electrolyte under the most favorable conditions, in regard to the reducing action at the cathode; the variation of conditions, such as electrodes, temperature,

current density, concentration, and separation of anolyte and catholyte. It is therefore obvious that the results obtained by Sherard-Cowper-Coles are erroneous, as well as the statement of Gustav Gin that he obtained metallic vanadium by Cowper-Coles method. (Transactions of the American Electrochemical Society, **16**, 439.)

Both authors evidently mistook platinum hydride, which may vary in color from light gray to black, for vanadium. By testing the conductivity of the cathode deposit, and by ignition in the flame of a Bunsen burner, it was proven in later experiments, in which the same deposit occurred, that it was platinum hydride. The measurement of the resistance between equal distances over the surface of the platinum cathode, by means of a millivolt potentiometer, *i. e.*, the voltage drop between the ends of two wires, one centimeter apart, was 11 millivolts at all points on the surface of the cathode. As the film was very thin, not much stress can be put on the conductivity test.

Experiments Nos. 10 and 53 were repeated, being run for two hours and ten minutes each; the electrodes were tested in the manner described above. The results were as follows: The cathode of No. 10 at the start weighed 5.8006 grams, and after electrolysis 5.8008 grams. The increase in weight was 0.0002 gram. After ignition the weight of the cathode was identical in appearance with that of the original electrode.

The cathode of No. 53 at the start weighed 5.8006 grams. After the electrolysis the weight was between 5.8007 and 5.8008 grams. After igniting, the weight of the cathode was 5.8006. In both cases the electrodes after ignition were perfectly bright, showing no indications that there had been any deposition. These tests prove clearly that the deposits obtained were platinum hydride, and not metallic vanadium.

Experimental Work—Part II.

Electrolysis of Solutions of Mixed Salts. A series of 112 experiments were performed on electrolytes containing another salt besides the vanadium compound. The method of J. Koppe and E. C. Behrendt for the preparation of double salts was tried. This method for producing the double sulphate consists in dis-

solving metavanadic oxide in an excess of dilute sulphuric acid, and reducing the solution with sulphur dioxide gas. To this reduced solution is added an excess of the sulphate with which the vanadium is to form the double salt, and the solution then carefully evaporated first on the water bath, and finally at a higher temperature. A voluminous deposit is obtained, light blue in color. The mother liquor is poured off, and powdery blue mass put into a large volume of water. The double salts of vanadium are not very soluble, so settle out, and may be easily filtered. The following double sulphates of vanadium were prepared: ammonium, calcium, magnesium and aluminium, but as they were found not to be very soluble, their solutions were valueless as electrolytes. (J. Koppe and E. C. Behrendt: "Zeitschrift für anorganische Chemie," **35**, 154-186.)

As the double salt solution of vanadium could not be used for electrolytes, other means had to be employed to study the effects of various inorganic salts on the electrolysis of vanadium compounds. This was accomplished by adding the salts in question to a solution of some vanadic salt such as the sulphate, fluoride, etc. The results are tabulated in Tables II to VI.

Summary of Conclusions. In a majority of the tests made a black film was formed on the cathode wherever platinum was used. This coating, on careful washing, gave no indication of the presence of vanadium.

Carbon anodes, when used in connection with mercury cathodes, or with the vanadium fluoborate or fluosilicate disintegrate.

Monel metal cathodes are unsatisfactory, in that they are readily attacked by the electrolytes, the nickel being attacked and the copper remaining in a finely divided form. These electrodes show a decrease in weight after the electrolysis.

In Experiments Nos. 87 and 88, Table IV, where a porous cup was used, a definite cathode deposit formed. The catholyte was a solution of the mixed vanadic (V_2O_5) sulphate, and magnesium sulphate. The deposit was grayish-brown, and non-homogeneous, composed of brown and white particles. The analysis of the deposit is 24.88 percent metallic magnesium and 25.46 percent vanadic oxide (V_2O_5). The formation of this deposit was slow, only 0.6875 gram being formed during the run of four hours.

The electrolyte of the mixed vanadic and ammonium sulphate is ordinarily reduced to the blue vanadyl state (V_2O_4). When boric acid (B_2O_3) is added to saturation, the reduction at the cathode continued to the green sesquioxide form (V_2O_3).

Electrolytes containing the mixed vanadic and aluminium sulphates are generally reduced to the green sesquioxide state (V_2O_3). With a high current density (0.76 to 2.01 amperes per sq. in. or 0.12 to 0.31 amp. per sq. cm.), the electrolyte used as catholyte in a porous cell, with a platinum cathode, was reduced to the lavender state, corresponding to the oxide V_2O_2 or VO. This phenomenon is independent of the temperature.

The mixed vanadic and magnesium sulphate electrolytes were generally reduced to the blue vanadyl state (V_2O_4) if a low current density was employed. The reduction proceeds to the green sesquioxide form (V_2O_3) by high current densities at cathode. This occurs whether a porous cup is used or not, and the intensity of the reduction increases with the rise in temperature.

Vanadium fluoborate and vanadium fluosilicate electrolytes are limited in their state of reduction to the blue vanadyl form (V_2O_4). The original green or yellowish-green of both these electrolytes is due to a partial reduction from the yellow vanadic to the blue vanadyl form, both mixing and giving a green color to the original electrolyte. This green color must not be mistaken for the sesquioxide green color.

The sesquioxide state of vanadium electrolytes can only be reached by first passing through blue vanadyl state (V_2O_4). This fact may be readily observed in the course of electrolysis experiments, Nos. 47 and 48, Table III.

Experimental Work—Part III.

Salts with Acids. The incentive to this thesis was originally given by a series of approximately one hundred experiments on acid electrolytes containing vanadium, which were performed at the Colorado School of Mines and Lehigh University during the years 1910 to 1915. The idea was to devise a hydro-electrolytic method for obtaining vanadium from carnotite concentrates, and concentrates from vanadic sandstones. All the tests made were negative, in so far as obtaining a deposit of vanadium by

electrolysis was concerned. The electrolytes employed were acid solutions, obtained by leaching the concentrates extracted from carnotite and vanadiferous sand-stones with dilute solutions of different acids. The concentrates were collected by a process of attrition and the separation of the vanadium mineral from the gangue by flotation (S. Fischer: "The concentration of carnotite ores and some similar ores," Met. and Chem. Eng., **10**, 356 to 359 (1912).

Only one set of tests is of interest; the tests for which dilute nitric acid was employed as the leaching agent. The electrolyte used was prepared as follows: 10 grams of carnotite concentrates, containing 12 percent V_2O_5, was leached with 10 c.c. of concentrated nitric acid made up to 100 c.c. with water. A dark green solution was obtained, having specific gravity of 1.10 at 32° C. This solution, upon being electrolyzed, turned yellow, and the specific gravity was reduced during electrolysis from 1.08 to 1.06. Under these conditions, at a temperature between 20.1° and 25° C., a yellowish-brown precipitate separated from the solution, which proved to be a hydrated oxide of vanadic acid. On testing the solution for vanadium, not a trace could be found.

In the following 123 experiments, both organic and inorganic acids were used to form salts with vanadic acid, and the solutions subjected to electrolysis, varying current density, temperature, concentration and electrodes, both with and without the use of a porous partition. See Tables VII to XII, inclusive.

Conclusions. After investigating a number of inorganic and organic acids as solvents for vanadic acid, it may be said that none act satisfactorily as electrolytes for obtaining electrode deposits. The reduction at the cathode was insufficient to reduce the salt to the metallic form.

Vanadic acid, dissolved in dilute hydrochloric acid, gives a greenish-yellow solution which on electrolysis passes from this green color, through the blue vanadyl state (V_2O_4) to the green sesquioxide state (V_2O_3). If a platinum cathode is employed, a gray to black film is formed, varying in amount and tendency towards a black color, directly as the time and the current density. This deposit contains no vanadium, it being a coating of platinum hydride.

If dilute sulphuric acid is employed as solvent for vanadic oxide (V_2O_5) a yellow solution is obtained. This on electrolysis is reduced to the blue vanadyl state (V_2O_4) giving no deposit containing vanadium on either cathode or anode.

Dilute nitric acid only dissolves very little vanadic oxide (V_2O_5) (less than 0.5 gram V_2O_5 per 100 c.c. of dilute acid). The amount of vanadic oxide dissolved varies only slightly with the concentration of the nitric acid. The concentrations employed were: 1 to 1, 1 to 2, 1 to 3, 1 to 4, and 1 to 5 parts by volume of concentrated nitric acid to parts water. In no case was more than 0.5 gram of vanadic acid dissolved in 100 c.c. of the solvent.

A dilute hydrofluoric acid solution of vanadic oxide has a yellowish-green color. On electrolyzing the solution is reduced to the vanadyl state (V_2O_4). No deposition takes place when a platinum cathode is employed. A monel metal cathode was partially attacked, nickel going into solution, leaving non-adherent particles of copper, similarly as in Experiments Nos. 34, 44 to 47, Part I.

Vanadic oxide dissolved in a dilute solution of lactic acid gives the blue vanadyl color, which does not show any further reduction on electrolysis. This original blue coloration is evidently due to the organic acid used, reducing the vanadic acid and forming the vanadyl lactate. Where no porous partition was employed to keep the anolyte and the catholyte separate, a black film of platinum hydride formed on the platinum cathode, the catholyte being the vanadyl lactate solution. On using a porous partition, a brown, very thin coating was formed on the platinum cathode, which on ignition gave forth an organic odor. The globular residue left after ignition dissolved with a yellow color in sulphuric acid and gave a test for vanadium. The residue was fused vanadic acid.

A solution of vanadic oxide in dilute ethyl sulphuric ($C_2H_5 . HSO_4$) acid, has a light green color which, on electrolysis, changes to the blue vanadyl state (V_2O_4). No deposit is formed on the platinum cathode, whether a porous cup is used or not.

Vanadic oxide dissolves, giving a blue colored solution (in dilute tartaric acid), the intensity of the blue color depending on the amount of vanadic oxide dissolved. No change in the

color of the electrolyte was noticed in eighteen experiments made with varying concentrations from 0.014 to 0.448 gram of vanadic acid per c.c. Neither the current density variations, 40 to 161 amperes per sq. ft. (4.4 to 18 amp. per sq. dm.) nor the temperature changes (20° C. to 98° C.) had any further reducing effect on the electrolyte. Also, under these same conditions, no deposit of vanadium formed on either the anodes or the cathodes.

On using concentrated acids as solvents for vanadic oxide, it was observed that the amount of vanadic oxide dissolved in the different concentrated oxides was not the same. Concentrated hydrochloric acid (sp. gr. 1.18 to 1.19) dissolved 0.133 gram vanadic acid per c.c. Concentrated sulphuric acid (sp. gr. 1.84) dissolved 0.02 to 0.304 gram vanadic oxide per c.c., depending on the purity of the vanadic oxide used, or the temperature of the solvent, and on the amount of water absorbed by the sulphuric acid. A very small amount of moisture in the concentrated sulphuric acid causes a rapid increase in the mount of vanadic oxide dissolved. Concentrated nitric acid (sp. gr. 1.42 to 1.425) practically dissolves no vanadic oxide when cold, and only very little when hot, much less than 0.0025 gram of vanadic oxide being dissolved in 1 c.c. of the hot concentrated nitric acid. Vanadic oxide dissolves to the extent of 0.81 gram per c.c. in concentrated lactic acid (sp. gr. 1.21) when hot. On cooling, a voluminous precipitate separates from the solution which, on ignition, emits an organic odor. On slowly heating, an odor peculiar to lactic acid is given off, indicating that the compound is evidently the vanadyl lactate.

In electrolyzing a solution of concentrated hydrochloric acid saturated with vanadic acid, a reduction of the electrolyte occurs, ranging from an originally greenish-blue, through blue to the green sesquioxide state (V_2O_3). When a platinum cathode is used a gray to black film is formed, showing no vanadium. This cathode deposit was found to be platinum hydride. If a carbon anode and a platinum cathode are employed a — E. M. F. of 0.025 volt is obtained. On the other hand, using a lead and a carbon electrode a + E. M. F. of 0.1 volt, indicates that the lead in this case acts as anode.

The electrolysis of concentrated sulphuric acid (sp. gr. 1.84) saturated with vanadic oxide, gives a green salt deposit on the

cathode. In all the literature on vanadium up to date no indication could be found that this had been done. Brierley, in 1886, electrolyzed a solution containing vanadyl oxide (V_2O_4) in dilute sulphuric acid, using it as the catholyte in a porous cup. He obtained the sesquioxide solution, green in color, corresponding to the salts of the oxide (V_2O_3). This green solution was then treated with strong sulphuric acid of twice its volume. After standing for twenty-four hours a green precipitate separated, having the formula "$V_2O_3(SO_3)_4.9H_2O$," according to Brierley. In the same paper mention was made of the fact that this salt could not be isolated, due to its being so readily oxidized. It is, therefore, rather difficult to say whether the formula given by Brierley is an assumption, or whether the product was actually analyzed. Brierly, J. Chem. Soc., **49**, 822 to 824 (1886).

It was found that, under no condition was it possible to determine the composition of the green sulphate salt, as this compound was very soluble in the water or the alcohol required for washing. The wash solution in each case showed the blue vanadyl color (V_2O_4). Even ether dissolved some of the green sulphate salt as soon as it mixed with the concentrated sulphuric acid adhering to the small crystals of the deposit.

Attempts were made to obtain the green sulphate deposit on the cathode. It was freed from the adhering acid as well as possible by washing very quickly with water. The salt was then dissolved in water and recrystallized. As soon as water was used, the salt was oxidized to the blue vanadyl state, and the analysis was then made on this product. In alcohol the green deposit also dissolved, giving a blue colored solution. The analysis of the blue salt obtained after recrystallizing from the aqueous solution and drying at 100° C. gave the following analysis: 42.54 percent V_2O_4 and 43.83 percent SO_3. This composition did not coincide with the composition of any of the sulphates in the literature, and the blue salt was dissolved and recrystallized four times and the product again analyzed, and found to contain 42.56 percent V_2O_4 and 40.49 percent SO_3.

It was found that the vanadium content in both instances checked. The SO_3 content in the second case, however, was lower. This was evidently due to the fact that in the first case not all free sulphuric acid had been eliminated by washing. On

comparing these results with the vanadyl sulphates known it was found that the ratio of V_2O_4 to SO_3 equals 1 to 0.953 for the salt $VOSO_4.2H_2O$. The same ratio in the second analysis is V_2O_4 to SO_3, equals 1 to 0.952. This was evidently the salt formed, the difference in percentages being due to partial elimination of the water of crystallization.

In other ways the recrystallized blue sulphate salt behaved like the compound $VOSO_4.2H_2O$. For instance, on evaporating an alcoholic solution containing the salt, the blue crust left swells, giving the whole a blistered appearance. The crust after grinding was not readily soluble in cold water, but remained suspended like powdered aluminium. The blue powder formed from the blistered crust obtained from the alcoholic solution after evaporation, is made up of small plates (microscopic) and in moist air deliquesces to a thick blue syrup. It may be concluded, therefore, that the salt obtained by electrolysis is a sesqui-vanadium-sulphate, which on dissolving in water gives the vanadyl sulphate $VOSO_4.2H_2O$ on evaporation.

A hot concentrated solution of lactic acid, saturated with vanadic oxide, has so low an ionization that the electric current does not pass, even on putting the cell directly across the terminals of 120 volt D. C. source.

Regarding the electrodes, it may be said that carbon anodes in concentrated sulphuric acid electrolytes disintegrate, and that lead anodes become coated with a film of sulphate, thus increasing the resistance to such an extent as to make the passage of the electric current difficult. Lead cathodes in concentrated and dilute hydrochloric acid electrolytes tend to become coated with lead chloride, which was observed in every instance where such electrodes were used in this solution. The lead chloride, being very insoluble, collected at the bottom of the receptacle.

It was ascertained in the course of these investigations that the black deposit, which formed on the platinum cathodes, was platinum hydride which, under certain conditions, such as low current densities and the short duration of time for the passage of the electric current, will give a light gray coating, metallic in appearance which, if not carefully investigated, might be taken for a deposit, such as metallic vanadium. Upon increasing the length of time for the passage of the current, such deposits increase

somewhat in thickness, giving the deposit a dark gray to black color. The color and thickness of the coating is also directly proportional to the current density, it increasing as the current density is increased.

Experimental Work—Part IV.

As vanadium in many respects resembles antimony and arsenic, it was thought likely that it would be deposited from a similar electrolyte. (Table XIII).

Conclusions. Vanadium cannot be deposited from an alkaline sulphide electrolyte, such as is used in the electro-deposition of antimony.

Experimental Work—Part V.

The Alkali Vanadate Electrolytes and the Anode Reaction. Vanadium forms a large number of acids, of which the most important ones are the ortho (H_3VO_4), the meta (HVO_3) and the pyro ($H_4V_2O_7$) vanadic acids. In addition to these, vanadium forms polyacids. The series of salts formed from the various types of vanadic acids exceeds those of any other inorganic element. In forming ortho, meta and pyro acids, vanadium resembles silicon, phosphorus and arsenic.

The vanadic acid (V_2O_5) of commerce is the anhydride of metavanadic acid HVO_3. ($2HVO_3 = H_2O + V_2O_5$).

Vanadic acid occurs in three modifications: the two yellow and red amorphous forms, and the gray crystalline form. The yellow amorphous form is a powder, golden to orange yellow in color. It is partly soluble in water, one liter of water dissolving approximately 300 milligrams. The red modification is amorphous and brick-red in color. It is slightly more soluble in water than the yellow form, its maximum solubility being about 500 milligrams per liter. The crystalline form is obtained by fusing either of the amorphous modifications, giving a dark gray, brittle crystalline mass. This mass, when finely ground, is dark red in color. In the melted form, the crystalline vanadic acid acts readily on the container in which it is fused, attacking even platinum. Fused in silica ware, it forms silicates; and when fused in carbon containers it forms carbides. The three modifications dissolve

in dilute hydrochloric and dilute sulphuric acid. The sulphate solution is yellow colored, and the hydrochloric acid solution is yellow to yellowish-green. Dilute nitric acid has little solving effect on vanadic acid. In water the amorphous modifications give a yellow solution. Vanadic acid dissolved in concentrated hydrochloric acid gives a dark bluish-green solution; dissolved in concentrated sulphuric acid a brownish-yellow solution is obtained. Concerning the alkali-hydrates, vanadic acid is most readily soluble in sodium hydrate; to a lesser degree in potassium hydrate, and very difficultly soluble in ammonium hydrate. One of the best solvents of vanadic acid is a solution of sodium peroxide containing hydrogen peroxide. A very good summary on the chemistry of vanadium and its salts is given by Warren F. Bleecker, in his article "Notes on the Chemistry and the Metallurgy of Vanadium," Part I. (Met. and Chem. Eng., **8**, 666-671 (1910)).

Of the many possible alkali vanadates, only one form is of importance, the metavanadates. The ortho, pyro and the intermediate vanadates very readily transform into the stable meta modification, liberating alkali at the same time.

A series of 33 experiments was run on the sodium metavanadate, in order to study the effects produced at the cathode, the anode and in the electrolyte. The sodium metavanadate used in these tests was obtained from Merck and Company, and was chemically pure.

In experiments Nos. 1, 2 and 3 an electrolyte containing 0.007 gram of sodium vanadate ($NaVO_3$) per c.c. was electrolyzed between a platinum cathode and a carbon anode. The anode current density varied between 12 to 19 amperes per sq. ft. (1.3 to 2.1 amp. per sq. dm.) and the temperature ranged from 20° C. to 74° C. The platinum cathode showed a dark film, giving no test for vanadium: it was platinum hydride. The increase in weight of the cathode due to this black film was 0.0003 gram. On ignition of the cathode in the flame of a Bunsen burner and reweighing, it was found that the cathode weighed the same as at the start of the experiment. The anode gave indication of a slight deposit, reddish in color, which dissolved in the course of electrolysis, giving the electrolyte an orange yellow color.

The same electrolyte was used for experiments Nos. 4 to 7, but instead of using a carbon cathode, a platinum wire was em-

ployed, and boric acid was added to the solution to saturation. The anode current density ranged from 33 to 164 amperes per sq. ft. (3.6 to 18 amp. per sq. dm.), and the temperature ranged from 18° to 113° C. The results obtained coincided with those for tests Nos. 1, 2 and 3.

In experiments Nos. 8, 9 and 10 the electrolyte was of the same concentration as in experiments Nos. 1, 2 and 3, but saturated with boric acid. The anode current density corresponded to that used in those experiments, but the temperature was only permitted to rise to 69° C. The results obtained corresponded in every detail to those in experiments Nos. 1 to 7.

The electrolyte of experiments Nos. 11 to 17 contained 0.007 gram of sodium metavanadate per c.c. to which was added approximately 0.0001 gram of an addition agent. The agents used were glue, quinoline and tannic acid. The current density varied from 24 to 115 amperes per sq. ft. (2.6 to 13 amp. per sq. dm.). The temperature range was from 25° to 99° C. Both electrodes were of platinum, the cathode being a No. 18 B. & S., so as to promote the oxidizing action at the anode. The anode showed a slight red deposit of vanadic oxide. Platinum hydride formed on the wire cathode. The electrolyte changed from a colorless to an orange yellow solution, the color change starting at the anode.

In experiments Nos. 18 to 21 the electrolyte contained 0.007 gram of sodium metavanadate per c.c. and was saturated with boric acid. Glue and quinoline were tried as addition agents, being added to the extent of 0.0001 gram per c.c. of electrolyte. The results obtained in these tests were identical with those of experiments Nos. 11, 12, 13 and 14, the presence of these organic addition agents having no effect upon the results of the electrolysis.

Experiments Nos. 22 to 33 involved a change in concentration of the electrolyte. In Nos. 22 to 25, the electrolyte contained 0.143 gram of sodium metavanadate per c.c.; Nos. 26 to 29 the concentration was 0.076 gram per c.c., and in Nos. 30 to 33 the concentration was 0.036 gram per c.c. The anode current density used in each case was from 24 to 196 amperes per sq. ft. (2.6 to 21.6 amp. per sq. dm.). The temperature ranged from 18° to 97° C. The electrodes were a carbon anode and a platinum

cathode. As in the previous experiments, the colorless electrolyte changed to orange red, starting at the anode. The red deposit on the anode seemed to remain only after the electrolyte had been completely changed to the yellow state. Platinum hydride formed on the cathode.

In an article published by Warren F. Bleecker entitled, "Notes on the Chemistry and Metallurgy of Vanadium," the author gives a brief outline of an electrolytic method for obtaining vanadic oxide. He used a porous cup in which the anolyte was contained. The anolyte is a solution of sodium metavanadate in water. Its concentration was 0.2 gram vanadic oxide (V_2O_5) per c.c. The catholyte was water containing a small amount of sodium hydroxide. The anode was platinum and the cathode iron or copper. The anode current density used was 30 amperes per sq. ft. (3.3 amp. per sq. dm.) at the anode. Bleecker states that "without taking more than the usual precautions, the grade of the anode product should be 98 percent V_2O_5, the impurities being principally lime and silica." Bleecker: "Notes on the Chemistry and Metallurgy of Vanadium," Part III. (Met. and Chem. Eng., **9**, 503-504 (1911)).

Bleecker not only deserves all the credit for having done the most valuable work in the recent development of the metallurgy of vanadium, but he also was the first to devise the electrolytic method for obtaining vanadic oxide on a commercial basis from sodium metavanadate electrolytes. It is only to be regretted that Bleecker did not give more detailed information concerning the reactions taking place during electrolysis, and the efficiency of his process. It was therefore thought of value to investigate the reactions taking place in the course of electrolysis of metavanadate solutions and to study the efficiency of the process.

An endeavor was made to prepare a sodium metavanadate electrolyte according to the equation $V_2O_5 + 2NaOH = 2NaVO_3 + H_2O$ by digesting 20 grams of pure vanadic oxide in 100 c.c. solution of 8.79 grams sodium hydroxide. The vanadic oxide (V_2O_5) used was 99.93 percent V_2O_5, and the sodium hydroxide was 98 percent pure. In order to obtain an electrolyte which would contain 0.2 gram of vanadic oxide per c.c. it required therefore 20.02 grams of vanadic oxide (99.93 percent pure) and 8.97 grams sodium hydroxide (98 percent pure). It was found, however,

that this amount of sodium hydrate was not sufficient to dissolve the vanadic oxide. At first some of the oxide went into solution; then further additions were simply changed to the grayish-green

a Fig. 1. b

vanadium hydroxide, and when the last of the vanadic oxide was added, a large bulk of the vanadium hydroxide remained undissolved. Enough sodium hydroxide was then added to give a clear

solution. It required 22.72 grams of sodium hydroxide (98 per-cent pure) in 100 c.c. of water to dissolve 20.02 grams vanadic oxide giving a clear solution at 70° C.

Electrolytes of this composition (0.2 gram of vanadic oxide and 0.2 gram of sodium hydroxide per c.c.) were then used in experiments Nos. 34 to 40. The electrolyte was strongly alkaline and had a faint yellow appearance.

In experiments Nos. 34, 35 and 36 a porous cup was used as diaphragm. The anolyte was the metavanadate solution, as described above, while the catholyte was water containing approximately 0.01 gram of sodium hydroxide per c.c. The anode was platinum and the cathode carbon. The anode current density was 15 amperes per sq. ft. (1.7 amp. per sq. dm.). The temperature varied from 18° to 93° C. In test No. 34, the anolyte was practically colorless at the start, but slowly changed in color through faint yellow to lemon yellow, and after two hours and eighteen minutes was dark orange. A thin, brick-red layer of hydrated vanadic oxide formed on the anode, which on drying at 110° C. weighed 0.1253 gram. On fusing this deposit on the platinum anode, it lost 0.0073 gram, giving the crystalline form of vanadic oxide, which weighed 0.1180 gram. The deposit before and after fusion was hygroscopic, but to a much greater extent before fusion had taken place.

The electrolyte left from experiment No. 34 was used as anolyte in a porous cup in experiment No. 35. The anode current density was the same as in No. 34, and the temperature ranged from 66° to 68° C. The anolyte was orange yellow at the start, and remained so during electrolysis. The deposit on the anode was brick-red in color and adhered to the anode in layers (see Fig. 1a). The deposit weighed 2.7938 grams after drying at 110° C., and 2.727 grams after ignition. The test ran for 4 hours and 13 minutes.

Experiment No. 36. A fresh portion of the same electrolyte as was used in experiment No. 34 was neutralized with boric acid and used as anolyte for experiment No. 36. The anode current density employed was 15 amperes per sq. ft. (1.7 amp. per sq. dm.). The temperature ranged from 83° to 93° C A porous cup was used as a diaphragm to separate anolyte and catholyte. The electrolysis lasted for six hours and forty minutes. At the

start of the test the anolyte was lemon yellow in color, due to the neutralization of the colorless sodium metavanadate solution with boric acid. After one hour and thirty minutes the anolyte was orange yellow in color. The weight of the anode deposit was 7.058 grams unignited and 6.3647 grams upon ignition.

As the anode ampere efficiency is considered in all of the previous and the following experiments, its theory is most conveniently treated in this place. According to Düllberg the metavanadate of sodium in solution is present as three combined molecules of sodium metavanadate ($NaVO_3$), corresponding to $Na_3V_3O_9$. He determined this fact by conductivity tests and by ascertaining the neutralization curves. Düllberg: "Concerning the Behavior of Vanadates in Solution." (Z. für phys. Chem., **45**, 129 and 182.

The reaction taking place during electrolysis of the sodium vanadate is in all probability as follows: $2Na_3V_3O_9 = 3(V_2O_5 + O) + 6Na$ followed by the secondary cathode reaction $6Na + 6H_2O = 6NaOH + 3H_2$.

During the electrolysis of a sodium metavanadate electrolytes, when using porous cup partitions hydrated vanadic oxide ($V_2O_5.xH_2O$) and oxygen formed at the anode, and hydrogen was liberated at the cathode with an increase in alkalinity of the catholyte. Düllberg does not explain the reactions in the electrolysis, confining himself only to the state in which sodium metavanadate exists in solution. The reaction in electrolysis is evidently first a polymerization of the simple $NaVO_3$ molecules to the molecule $Na_3V_3O_9$, and then the splitting up of this complex molecule into sodium and vanadic oxide plus oxygen. The sodium then combines with the hydroxyl radical (OH) obtained from the decomposed water, giving sodium hydroxide in solution, while the hydrogen is liberated at the cathode.

The question now arises, what is the valency of the vanadic oxide in this connection: two molecules of the polymerized sodium metavanadate may be written in two ways: $2Na_3V_3O_9$, or $Na_6V_6O_{18}$. This latter formula may be simplified by dividing through by 3, giving the formula $Na_2(V_2O_6)$. The radical V_2O_6 is undoubtedly the one appearing at the anode, but is further split up into $V_2O_5 + \frac{1}{2}O_2$. The radical V_2O_6 is di-valent, there-

fore in calculations of the anode efficiency in the precipitation of sodium metavanadate solutions V_2O_5 may be considered di-valent.

As regards the anode deposit itself, it is best to base the ampere efficiency calculations on the ignited product, as it is very difficult to rid the original product from the accompanying water, giving a very uniform product upon which to base calculations. The unignited product is very hygroscopic, absorbing moisture so rapidly that weighing it is difficult. On heating the original deposit in a beaker immersed in nearly boiling concentrated sulphuric acid for ten hours, and then weighing in a closed receptacle, such as a weighing bottle, it was found that the loss in weight was practically identical with the loss obtained on fusing the deposit. For this reason it was determined to base the efficiency calculations on the weight of the fused product. It may be stated here that the loss in weight on ignition varied between 5 and 10 percent, practically the same figures holding true for the material dried at approximately 300° C. for a long time. This variation in percentage loss in weight is due to the hygroscopic property of the deposit itself, which causes a variation in the original weight of the substance taken for analysis, not every sample of the various anode products contained the same amount of water after drying at 110° C. Most of the anode products were analyzed. The greatest variation was again shown by the product dried at 110° C. On analysis of a large number of samples of the original anode deposit, it was observed that the vanadic oxide (V_2O_5) content varied between 83.33 percent and 90.11 percent. If it is considered that $V_2O_5.H_2O$ contains 91 percent vanadic oxide and knowing that the product is hygroscopic, one is quite justified in assuming the original deposit to be of the type $V_2O_5.\times H_2O$.

The results obtained on the original product when heated at approximately 300° C. for a long time, and on the fused product, checked very closely. The percentage of vanadic oxide content varied between 97.76 and 93.37 percent. A higher vanadic oxide content of either dried or fused product was never obtained in the course of the investigation. The product was always slightly contaminated with lime and silica from the porous cup, especially so if a part of the deposit dropped to the bottom of the cup, which very frequently was the case. It was regularly observed that,

after running a test, the inside of the porous cup had been attacked, becoming slimy, and a fine white material collecting at the bottom of the cup. This proved to be silicate of lime.

The ampere efficiency calculation is made according to Faraday's Law.

$\frac{\text{Molecular weight}}{\text{Valency}} \times 0.00001035 \times$ number of coulombs. This gives the theoretical amount deposited in a certain time. Therefore

$\frac{\text{Weight of product found}}{\text{Theoretical weight}} \times 100 =$ percent ampere efficiency.

In this instance the product chosen as a basis of calculation is the one of 98.4 percent purity, because it is unlikely that on any further refinement of the process, such as non-attackable porous cups, a less pure product would be obtained. Taking experiment No. 48, for example, the ampere efficiency figures out as follows:

$\frac{182}{2} \times 0.00001035 \times 0.625 \times 15780 = 9.2896$ grams—therefore the anode ampere efficiency $= (9.1223 \div 9.2896) \times 100 = 96.63$ percent. For all the other experiments a similar calculation will give the corresponding efficiency, so that one calculation will suffice to show the mode of procedure.

The anode ampere efficiencies of experiments Nos. 34, 35 and 36 are as follows: 2.90 percent, 44.97 percent and 62.97 percent respectively. It is evident from these results that the ampere efficiency increases rapidly as soon as the yellow stage of the anolyte is reached, which is indicated in experiments Nos. 34 and 35.

In experiments Nos. 37 and 38, the concentration of the anolyte was 0.2 gram of vanadic oxide per c.c. The electrodes were both carbon. For test No. 37 an anode current density of 48 amperes per sq. ft. (5.2 amp. per sq. dm.) was used. The temperature ranged from 85° to 94° C. The test ran for 7 hours and 22 minutes. The anode ampere efficiency was 40.57 percent. In experiment No. 38 an anode current density of 72 amperes per sq. ft. (8 amp. per sq. dm.) was used, the temperature ranging from 89° to 94° C. The deposit in this case did not adhere readily to the anode, most of it collecting in the bottom of the porous cup, and some being in the anolyte in colloidal form. The filtering of such a colloidal solution is extremely difficult, much of the

precipitate passing through the filter. For this reason it was impossible to obtain an efficiency determination in experiment No. 38.

In experiment No. 40 a lead anode and a carbon cathode were employed. The concentration of the anolyte, which was in the porous cup, remained the same as in experiments Nos. 38 and 39. The anode current density averaged 16 amperes per sq. ft. (1.8 amp. per sq. dm.). The temperature varied from 87° to 94° C. Deposition on the anode started after three hours and twenty minutes. The anolyte at the start was faintly yellow and at the end was of orange color. The efficiency was not determined, as the anode deposit showed the presence of lead strongly. The lead in the product indicates that lead was dissolved from the anode and re-precipitated as lead peroxide with the vanadic oxide.

An endeavor was made to increase the ampere efficiency by hastening the formation of the yellow vanadium compound in solution by adding an oxidizing agent. What the orange yellow compound in the solution was could not be determined, but it was found that, on allowing the orange yellow solution to evaporate freely in the air, large orange-colored crystals were formed. These large crystals on analysis gave the following composition: V_2O_5 61.57 percent and moisture 27.44 percent. This composition corresponds very closely with the salt $Na_2O.2V_2O_5 + 9H_2O$. The crystals also corresponded in every other way with the properties attributed to this compound in the literature. The crystals weathered in moist air without losing their crystalline form. They are readily soluble in cold water, but difficultly so in hot, as they decompose, coating the crystals with a dark-red compound which is difficultly soluble, and prevents further action by the hot water. The salt is soluble in a solution of oxalic acid, giving a green color initially and ending with a blue, while CO_2 is given off, showing that the final solution is a reduction product.

While the main aim in experiments Nos. 41 to 46 was to obtain the orange-colored solution, in order to increase the current efficiency, the most startling observation was that, with only a few drops of a solution of hydrogen peroxide (3 percent by volume) the vanadic oxide (V_2O_5) was very readily dissolved by the theoretical amount of sodium hydroxide. In other words: instead

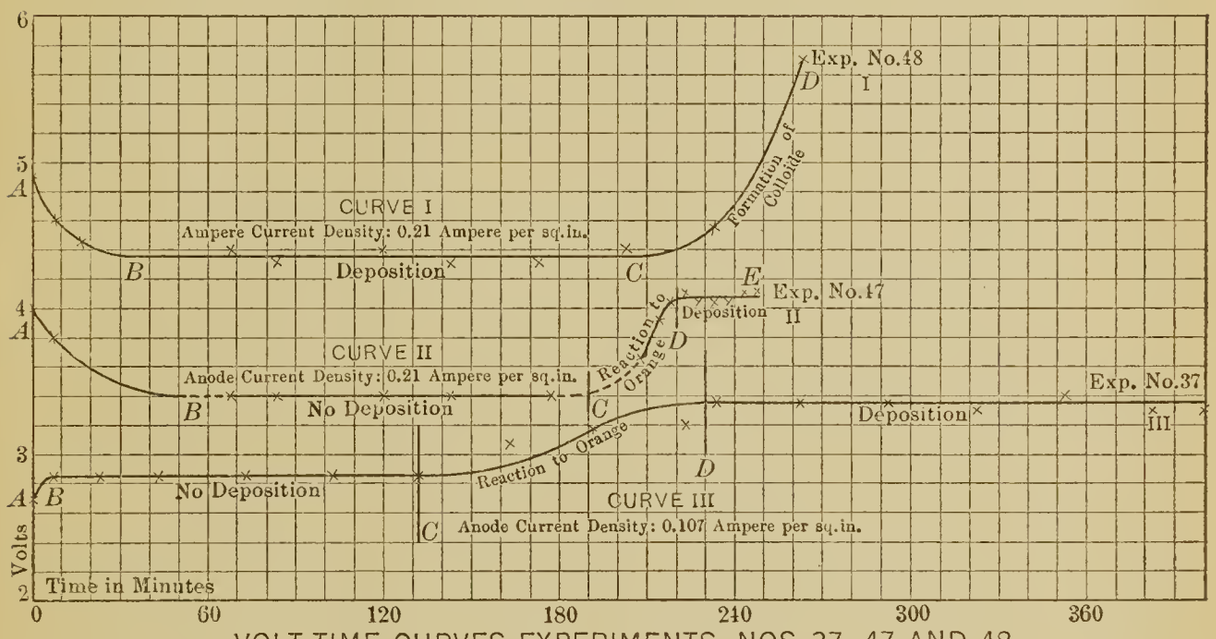
of taking 22.72 grams of sodium hydroxide to dissolve 20.02 grams of vanadic oxide, it required only 8.97 grams of sodium hydroxide (98 percent pure), when 5 c.c. of a 3 percent hydrogen peroxide solution was added, or a saving of 153.3 percent of sodium hydroxide. The solution of sodium metavanadate thus obtained acted practically neutral.

Electrolytes containing 0.2 gram of vanadic oxide (V_2O_5), 0.09 gram sodium hydroxide and 0.05 c.c. of 3 percent hydrogen peroxide solution per c.c. were used in experiments Nos. 41 to 46. The electrodes employed were a platinum sheet anode and a carbon cathode. A porous cup was used to contain the vanadium solution. The anode current density varied from 7 to 30 amperes per sq. ft. (0.8 to 3.3 amp. per sq. dm.) and the temperature ranged from 89° to 99° C. In all of these tests the anode ampere efficiency was markedly increased by the use of the hydrogen peroxide solution, varying from 92.78 to 96.46 percent. The variation in current efficiency is due to the fact that in some instances not quite enough hydrogen peroxide had been added to convert all of the sodium metavanadate over into the orange yellow compound. Experiments Nos. 41 to 45 were run for three hours, while No. 46 ran for three hours and fifteen minutes.

In experiments Nos. 47, 48 and 49, current efficiency comparisons were made between the electrolysis of a solution prepared by dissolving vanadic oxide in sodium hydroxide, and solutions prepared by use of hydrogen peroxide and of sodium peroxide as oxidizing agents. The anolyte used in experiment No 47 contained 0.2 gram vanadic oxide and 0.22 gram sodium peroxide per c.c. The anolyte for experiment No. 48 contained 0.2 gram vanadic oxide, 0.09 gram sodium hydroxide and 0.05 c.c. hydrogen peroxide (3 percent by volume). The anolyte used for experiment No. 49 was prepared by using, instead of hydrogen peroxide, 0.25 gram sodium peroxide (Na_2O_2) per c.c. of electrolyte.

In all three experiments platinum sheet anodes and carbon cathodes were employed, and a porous cup was used to separate the anolyte and the catholyte. The catholyte was a dilute solution of sodium hydroxide. The anode current density was 30 amperes per sq. ft. (3.3 amp. per sq. dm.), and the temperature varied between 90° and 99° C. In test No. 47 the anolyte was strongly alkaline, in No. 48 neutral and in No. 49 slightly alkaline. In

experiment No. 47 the orange color of the anolyte was obtained after three hours and forty minutes. A faint yellow color was observed after three hours and 10 minutes. It took, therefore, thirty minutes to obtain the full orange color after the first appearance of the faint yellow color, showing that when oxidation had started, the change from the faint yellow to the orange-colored solution progressed rapidly (see Curves I, II and III). The anode ampere efficiencies were as follows: 9.52 percent for experiment No. 47; 96.63 percent for experiment No. 48, and 85.89 percent for experiment No. 49. The anode deposit in each case was adherent and brick red in color. The analysis of the



VOLT-TIME CURVES EXPERIMENTS, NOS. 37, 47 AND 48.

Fig. 2.

fused products was as follows: the deposit of No. 47, 97.99 percent V_2O_5; that of No. 48, 98.37 percent V_2O_5, and that of No. 49, 98.21 percent V_2O_5. By use of the chemical oxidizing agents (H_2O_2 and Na_2O_2) deposition of the hydrated vanadic oxide formed immediately on the anode, independently of electrolytic oxidation.

In experiments Nos. 50, 51 and 52, potassium chlorate ($KClO_3$), potassium permanganate ($KMnO_4$) and chloride of lime ($CaOCl.Cl$) were used as oxidizing agents on an anolyte of the same composition as was used in experiments Nos. 47, 48 and 49. The amounts of the oxidizing agents required for the complete dissolving of 20.02 grams of vanadic oxide (V_2O_5) in 100 c.c.

of water containing the theoretical amount of 98 percent sodium hydroxide (8.97 grams of NaOH) was 3 grams potassium chlorate, 0.008 gram of potassium permanganate and 0.52 gram of chloride of lime. In order to give the most effective oxidizing conditions at the anode, a platinum wire (No. 18 B. & S.) cathode was employed. The anode was a platinum foil. The anode current density used was 30 amperes per sq. ft. (3.3 amp. per sq. dm.) and the temperature varied from 76° to 90° C. Porous cups were used as diaphragms to separate the anolyte and the catholyte. The three tests were run in series for two hours. The anode ampere efficiencies were 50.48 percent for experiment No. 50; 35.11 percent for experiment No. 51, and 63.7 percent for experiment No. 52. In test No. 50 it took one hour to obtain the orange yellow anode solution. In experiment No. 51 it was difficult to say what happened, because of the purple color imparted to the anolyte by the potassium permanganate, while in experiment No. 52 it required thirty-five minutes to obtain the orange coloration. This lag in obtaining the orange-colored anode solution accounts for the low ampere efficiency. The anode deposits in experiments Nos. 50 and 52 were adherent and brick red in color, while the deposit of experiment No. 51 was dark reddish brown and showed a tendency to form a colloidal solution.

In experiments Nos. 54 to 57 the variation in concentration of the anolyte contained in a porous cup was considered. The current density was changed in experiment No. 57, and in all cases lead sheet anodes were employed, while the cathodes were carbon.

In tests Nos. 54 and 57 the concentration of the electrolyte was the same, 0.2 gram of vanadium oxide per c.c. The anode current densities were 30 and 15 amperes per sq. ft. (3.3 and 1.7 amp. per sq. dm.) respectively, while the temperature range was from 90° to 97° C. The concentration of the anolyte of experiments Nos. 55 and 56 was 0.10 and 0.075 gram vanadic oxide per c.c. respectively. The anode current densities were 30 amperes per sq. ft. (3.3 amp. per sq. dm.). The temperature at which No. 56 was run was 90° C., while that of the test No. 55 varied from 66° to 71° C. The anode deposits were all contaminated with lead, so that the anode ampere efficiency was not determined. However, the effect of concentration is observed by considering the

weights of the deposits obtained in tests Nos. 54, 55 and 56, which are 5.6404; 3.2082 and 1.7146 grams respectively. That the anode ampere efficiency evidently decreases with the decrease in concentration of the vanadium anolyte is clearly shown by the yields obtained in the same length of time (2 hours and 15 minutes).

The concentration of the anolyte in experiments Nos. 58 and 59 was 0.2 gram of vanadic oxide per c.c. and 0.09 gram of sodium hydroxide per c.c. Ten c.c. of hydrogen peroxide (3 percent by volume) was added to the vanadium anolyte in test No. 58, and 0.25 gram of sodium peroxide to the anolyte of No. 59. Anolytes and catholytes were kept separated by the use of porous cups. The anode current density was 180 amperes per sq. ft. (20 amp. per sq. dm.) in each case, and the temperature ranged from 86° to 99° C. The anode ampere efficiency of test No. 58 was 84.22 percent, and that of test No. 59 was 80.29 percent. The tendency of the anode deposits in these two experiments was to form a colloidal solution, not so much of the vanadic oxide adhered to the anode as in cases where lower anode current densities were used. This to some extent explains the low current efficiency, as it was extremely difficult to obtain a perfect separation of the deposit and the solution by means of filtration, due to the colloidal state of some of the deposit itself. However, this loss would not make up the 12 percent difference between the yield of experiment No. 58 and experiment No. 48. The ampere efficiency evidently decreases with increase of the anode current densities above approximately 30 amperes per square foot (3.3 amp. per sq. dm.).

Experiments Nos. 60 to 62 involve chemically pure sodium metavanadate. The concentration was 0.2 gram of vanadic oxide per c.c. of water. A porous cup was used as a diaphragm to keep the anolytes and catholytes separated. The anode current density of Nos. 60 and 61 was 15 amperes per sq. ft. (1.7 amp. per sq. dm.), while in No. 62 the current density was 30 amperes per sq. ft. (3.3 amp. per sq. dm.). The temperature ranged from 87° to 99° C.

Experiment No. 60 indicates the length of time required to obtain the orange yellow solution. At the end of three hours the efficiency was only 8.76 percent, having taken two hours and 35 minutes before the orange yellow stage was reached. In test No. 61 the anolyte left from No. 60 was again electrolyzed for three

hours and 56 minutes. For this length of time the anode ampere efficiency was 96.29 percent, indicating again the necessity of having the vanadate anolyte in its higher state of oxidation (the orange yellow compound) in order to obtain a high anode ampere efficiency.

In experiments Nos. 63 to 66, sodium carbonate, sodium peroxide, potassium hydroxide and ammonia were tested as solvents for vanadic oxide. These solutions were then subjected to electrolysis, using them as anolytes in porous cups. The anolyte of experiment No. 63 was made by dissolving 15 grams of vanadic oxide (V_2O_5) in 100 c.c. of water containing 11.45 grams of anhydrous sodium carbonate (Na_2CO_3). The concentration of the anolyte in respect to the vanadic oxide was 0.15 gram per c.c. In order to obtain complete solution of the vanadic oxide, 10 c.c. of hydrogen peroxide (3 percent by volume) was added. The solution was practically colorless. The anode current density used was 30 amperes per sq. ft. (3.3 amp. per sq. dm.). The temperature ranged from 82° to 94° C. The anode deposit obtained was adherent and brick red in color, the anode ampere efficiency being 53.37 percent. The run lasted for three hours and 15 minutes, two hours and 20 minutes being required to reach the orange yellow state of the anolyte. The anolyte of experiment No. 64 was prepared by dissolving 15 grams of vanadic oxide in 100 c.c. of water containing 5.22 grams of sodium peroxide (Na_2O_2). No addition of hydrogen peroxide was made, as the vanadic oxide dissolved in the theoretical amount of sodium peroxide. The sodium peroxide evidently acted as oxidizing agent. The anode current density and the temperature range was the same as in experiment No. 63. The anode deposit was of brick red color and adhered to the anode in layers. The anode ampere efficiency was 93.58 percent.

In experiment No. 65 the anolyte was prepared by dissolving 13.99 grams of vanadic oxide in 100 c.c. of water containing 9.23 grams of potassium hydroxide. Thirty c.c. of hydrogen peroxide (3 percent by volume) was added to get complete solution. The catholyte was dilute potassium hydrate. The conditions of electrolysis were the same as in experiments Nos. 63 and 64, but the test was run for only one hour and 35 minutes. A deposit weighing 7.7 grams was obtained on the anode. This deposit was so

TABLE I. TESTS ON COWPER-COLES' ELECTROLYTE.

14.25 gm. Vanadic Acid (V_2O_5), 16.10 gm. Sodium Hydroxide, 259.20 gm. conc. Hydrochloric Acid. Made up to 2271 c.c. with distilled water.

No.	Concentration gm. per. c.c.	Electrodes		Area of Cathode in sq. in.	Volts	Amperes	Temperature		Current Density per sq. in.	Time	RESULTS	REMARKS
		Cathode	Anode				° C.	° F.				
1	0.0063	Platinum	Carbon	1.5	1.3 to 1.6	0.2	82	179.6	0.123	2 hr. 0 min.	No vanadium. Electrolyte reduced from yellow to blue (vanadic to vanadyl).	Cowper-Coles' original experiment. Electrolyte lemon yellow.
2	0.0063	"	"	1.5	1.7 " 1.8	0.4	82	179.6	0.246	1 " 34 "	" " " remained blue.	Electrolyte blue, when started, from test 1.
3	0.0063	"	"	1.5	1.25 " 1.3	0.1	82	179.6	0.0615	1 " 0 "	" " " " "	" " " " " " 2.
4	0.00315	"	"	2.06	1.9 " 2.0	0.265 to 0.27	82	179.6	0.129	1 " 15 "	No deposit. Electrolyte reduced, yellow, to green, to blue.	
5	0.00315	"	"	2.06	2.1 " 2.2	0.5	63 to 82	145.4 to 179.6	0.242	1 " 15 "	" " " " " " " " "	Temperature variation showed no effect.
6	0.00315	"	"	2.06	2.7	1.0	63 " 76	145.4 " 168.8	0.484	1 " 15 "	" " " " " " " " "	" " " " "
7	0.00315	"	"	2.06	3.2 " 3.5	2.0	76 " 80	168.8 " 176.0	0.968	1 " 25 "	" " " " " " " " "	" " " " "
8	0.0016	"	"	2.06	2.1	0.25	53 " 80	127.4 " 176.0	0.121	1 " 7 "	" " " " " " " " "	" " " " "
9	0.0016	"	"	2.06	2.6 " 2.9	0.50	80	176	0.242	1 " 15 "	" " " " " " " " "	Temperature constant.
10	0.0016	"	"	2.06	3.7 " 4.05	1.00	80 " 82	176 " 179.6	0.484	1 " 15 "	Thin black film on cathode; trace V. Electrolyte reduced as above.	
11	0.0016	"	"	2.06	5.6 " 5.8	1.9 " 2.00	82 " 85.5	179.6 " 185.9	0.947	1 " 15 "	" " " " " " " " " " "	Film did not increase in weight.
12	0.0008	"	"	2.06	3.15 " 3.3	0.25	52 " 70.5	125.6 " 158.9	0.121	2 " 20 "	No deposit. Electrolyte not reduced to blue; stayed yellow.	
13	0.0008	"	"	2.06	4.20 " 4.40	0.50	70.5 " 81	158.9 " 177.8	0.242	2 " 20 "	Same as 12.	
14	0.0008	"	"	2.06	6.2 " 6.4	1.00	81 " 83	177.8 " 181.4	0.484	2 " 20 "	" " " " grayish yellow due to finely divided carbon.	Carbon anode disintegrated, causing muddy appearance of electrolyte.
15	0.0008	"	"	2.06	11.0 " 12.5	2.00	82 " 83	179.6 " 181.4	0.968	2 " 20 "	" " 14.	" " " " as in 14.
16	0.0063	Lead	"	3.75	3.0	3.46 " 3.65	71.2 " 91	160.2 " 195.8	0.9 to 0.98	3 " 42 "	No deposit. Electrolyte reduced to blue.	Treeing on cathode. Temperature no effect.
17	0.0063	"	"	3.75	1.6 " 1.7	0.5	68 " 89.8	154.4 " 193.6	0.14	6 " 49 "	" " " " " "	" " " " " "
18	Same as 17 in every respect.											
19	0.0063	Lead	Carbon	3.75	1.81	1.0	81	177.8	0.28	0 " 35 "	" " " " " green-blue.	
20	0.0063	"	"	3.75	1.95	1.54	83	181.4	0.41	3 " 19 "	" " " dark green-blue. Not to vanadyl.	Endeavored to reduce to vanadyl blue color. Treeing.
21	0.0063	"	"	3.75	2.2 " 2.9	2.55	54 " 80	129.2 " 176	0.70	6 " 40 "	" " " reduced to green-blue. Reduction partial.	Used electrolyte from 20.
22	0.0063	Carbon	"	3.75	1.7	0.5	80	176	0.14	11 " 42 "	" " " " " vanadyl state.	
23	0.0063											
24	0.0063	"	"	3.75	2.1	1.5	80	176	0.28	1 " 22 "	" " " " " " "	
25	0.0063	"	"	3.75	2.35	1.5	80	176	0.41	3 " 19 "	" " From blue to green.	Carbon cathode gives better reduction. } Turned yellow-green on heating alone.
26	0.0063	"	"	3.75	2.8	2.5	62.3 " 73	144.1 " 163.4	0.70	0 " 30 "	" " Electrolyte at end yellow-green.	Electrolyte from 24.
27	0.0063	"	"	3.75	4.81 " 5.25	2.48 " 2.52	68.5 " 77	155.3 " 170.6	0.70	2 " 20 "	" " " not reduced; grayish-yellow.	Temperature effect is to lower reduction.
28	0.0063	"	"	4.5	2.5 " 3.15	3.5	71 " 95	159.8 " 203	0.80	3 " 22 "	" " " moss-green at end. No blue.	Neutralized with NaOH and added boric acid.
29	0.0063	Lead	Lead	3.75	2.5 " 3.15	0.5	41 " 90	105.8 " 194	0.14	12 " 2 "	" " " reduced; yellow-green-blue-lavender.	Reduction partial.
30	0.0063	"	"	3.75	2.53	1.00	80	176	0.28	0 " 55 "	" " " " to green.	Heavy treeing. Reduction one step further.
31	0.0063	"	"	3.75	2.97	2.0	80	176	0.56	2 " 0 "	" " " " " very dark green.	
32	0.0063	"	"	3.75	3.35	3.0	80	176	0.80	1 " 19 "	" " " " " " " "	Could not obtain vanadyl color. } Same electrolyte used.
33	0.0063	"	"	4.10	4.0 " 17.0	3.5	79 " 99	174.2 " 210.2	0.80	2 " 55 "	" " " " " " " "	" " " " " "
34	0.0063	Monel M.	Carbon	2.25	1.0 " 5.0	1.8 " 1.95	20 " 35	68.0 " 95.8	0.84	4 " 0 "	" " " " yellow-green-blue to lavender.	Treeing. High temperature, favors reduction to purple.
35	0.0063	Lead	"	3.75	1.65 " 1.7	0.5	39 " 85.5	102.2 " 185.9	0.14	11 " 37 "	" " " " to blue.	Monel metal disintegrated. Showing copper network and pits.
36	0.0063	"	"	3.75	1.87	1.0	76	168.8	0.28	1 " 38 "	" " Reduction of electrolyte, yellow-green-blue.	Electrolyte saturated with boric acid. Treeing.
37	0.0063	"	"	3.75	2.0 " 2.35	1.5	71 " 81	159.8 " 177.8	0.40	3 " 20 "	Same as 35.	" " " " " " } Temperature and C. D. no effect.
38	0.0063	"	"	3.75	2.15 " 3.2	2.5	47 " 81	116.6 " 177.8	0.70	5 " 41 "	" " 35.	" " " " " "
39	0.0063	"	"	3.75	2.5 " 3.8	3.5	70.3 " 86	158.5 " 186.8	0.93	2 " 55 "	" " 35.	" " " " " "
40	0.0063	Mercury	"	3.75	3.4 " 3.5	0.5 " 0.725	54.0 " 81.7	129.2 " 179.1	0.		" " 35.	" " " " " "
41	0.0063	"	"	3.75	4.05 " 4.2	1.54 " 1.575	79.0 " 83	174.2 " 181.4	0.		Cathode no V. Anode V_2O_5. Electrolyte became nearly colorless; gray-yellow.	Neutralized with NaOH and saturated with boric acid.
42	0.0063	"	"	3.75	4.7 " 5.1	2.58	65.0 " 79	149 " 174.2	0.	0 " 58 "	Same.	Same } To test for vanadium in cathode, the mercury was shaken with hot sulphuric acid (1:1), and the solution tested with hydrogen peroxide.
43	0.0063	"	"	3.75	5.3 " 5.6	3.50	65.0 " 80	149 " 176	0.	0 " 59 "	"	"
44	0.0063	Monel M.	Pt. Wire	2.25	2.0 " 2.1	0.25 " 0.34	20	68.0	0.11 " 0.15	4 " 0 "	Black deposit on cathode; no V, but showed Cu. Electrolyte—blue.	
45	0.0063	"	"	2.25	2.1	0.25 " 0.34	20	68.0	0.11 " 0.15	4 " 0 "	" " " " " " " " " " "	Quinoline. Monel metal disintegrated.
46	0.0063	"	"	2.25	1.75 " 1.95	0.25 " 0.35	20	68.0	0.11 " 0.15	3 " 50 "	" " " " " " " " " " "	Tannic acid. " " " } Cathode weighed and showed decrease in weight.
47	0.0063	"	"	2.25	1.60 " 1.95	0.25 " 0.35	20	68.0	0.11 " 0.15	3 " 50 "	" " " " " " " " " " "	Resorcine. " " "
48	0.0063	Platinum	Carbon	5.63	1.60 " 1.65	0.55	80 " 85	176 " 185	0.098	1 " 0 "	No V. No change in color of electrolyte.	Peptone. " " "
49	0.0063	"	"	5.63	1.8 " 1.9	0.9 " 1.0	85	185	0.16 " 0.18	1 " 0 "	Same as 48.	Reduced electrolyte with SO_2, was blue (vanadyl) at start.
50	0.0063	"	"	5.63	1.93 " 1.96	1.5	80	176	0.26	1 " 0 "	" " 48.	Same as 48. } Excess of SO_2 boiled out before electrolyzing.
51	0.0063	"	"	5.63	8.1	2.0	80	176	0.35	1 " 0 "	" " 48.	" " 48.
52	0.0063	"	"	3.00	5.25 " 6.1	0.5	20 " 70	68 " 158	0.16	1 " 7 "	No V. Electrolyte reduced to blue.	" " 48.
53	0.0063	"	"	3.00	9.3 " 9.5	1.0	25 " 33	77 " 91.4	0.33	0 " 27 "	Black film. Trace of V. Catholyte reduced to lavender.	Used porous cup. } Catholyte 100 c.c., Cowper-Coles Electrolyte. Anolyte 20 c.c., " " " + H_2O.
54	0.0063	"	"	3.00	15.3	2.0	33 " 56	91.4 " 132.8	0.66	0 " 40 "	Same.	" " "
55	0.0063	"	Pt. Wire	3.00	20. " 21.	3.0	56 " 76	132.8 " 168.8	0.99	0 " 49 "	Same.	" " "

| No. | Conductance in mho per c.c. | Electrodes | | Cathode in mm. | Volts | | |

Electrolyte I: 14.25 grams vanadic acid.
71.10 " 26% ammonia.
193.10 " conc. sulphuric acid.
Make up to 2271 c.c. with water.

TABLE II.

No.	Concentration V_2O_5 gm. c.c.	Electrodes: Cathode	Electrodes: Anode	Area of Cathode in sq. in.	Volts	Amperes	Temperature °C.	Temperature °F.	Current Density per sq. in.	Time	RESULTS	REMARKS
1	0.00627	Platinum	Carbon	1.5	1.6 to 2.2	0.2	51.0 to 85.	177.8 to 185.	0.133	2 hr. 0 min.	No deposit on cathode. Electrolyte, yellow to greenish-blue.	Without current forced through, obtained + 0.3 volts.
2	0.00627	"	"	1.5	2.3	0.4	82.	179.6	0.266	0 " 30 "	Same; to bluish-green.	
3	0.00627	"	"	1.5	1.3	0.1	81. " 82.	177.8 " 179.6	0.067	0 " 59 "	Same; to blue.	
4	0.00314	"	Pt. Wire	2.2	2.5	0.25	80. " 82.	176. " 179.6	0.114	1 " 15 "	No deposit. Electrolyte, yellow to green.	
5	0.00314	"	"	2.2	2.7 " 2.75	0.50	60. " 63.	140. " 145.4	0.228	1 " 15 "	" " " to green.	
6	0.00314	"	"	2.2	3.3	1.00	70. " 72.	158. " 161.6	0.456	1 " 15 "	" " " " "	
7	0.00314	"	"	2.2	4.40 " 4.20	2.00	40. " 46.	104. " 114.8	0.912	1 " 15 "	" " " " blue.	
8	0.00157	"	"	2.2	2.70 " 2.8	0.25	80.	176.	0.114	1 " 17 "	Same as 4.	
9	0.00157	"	"	2.2	3.2 " 3.1	0.50	60. " 64.	140. " 147.2	0.228	1 " 17 "	Nothing on cathode. Electrolyte, blue.	
10	0.00157	"	"	2.2	3.8 " 4.0	1.00	70.	158.	0.456	1 " 17 "	" " " " "	
11	0.00157	"	"	2.2	5.6 " 5.2	2.00	41. " 44.	105.8 " 111.2	0.912	1 " 17 "	Dark brown-black film on cathode. No V. Electrolyte blue.	
12	0.00079	"	"	2.2	3.15	0.25	80. " 86.	176. " 186.8	0.114	2 " 20 "	Nothing.	
13	0.00079	"	"	2.2	3.84 " 4.4	0.50	60. " 70.	140. " 158.	0.228	2 " 20 "	" on cathode. Electrolyte blue-green.	
14	0.00079	"	"	2.2	5.7 " 5.3	1.00	70. " 73.	158 " 163.4	0.456	2 " 20 "	" " " " blue.	
15	0.00079	"	"	2.2	8.0 " 8.4	2.00	42. " 45.	107.6 " 113.	0.912	2 " 20 "	" " " " "	
16	0.00627	Lead	Carbon	3.75	2.0 " 2.7	0.5	48. " 85.	118.4 " 185.	0.140	3 " 34 "	No vanadium on cathode. Electrolyte reduced from yellow to blue.	
17	0.00627	"	"	3.75	2.6 " 2.7	1.07	75.	167.	0.300	0 " 57 "	Same.	
18	0.00627	"	"	3.75	2.98 " 3.2	2.00	76. " 82.	168.8 " 179.6	0.53	1 " 0 "	"	
19	0.00627	"	"	3.75	3.3	3.00	82.	179.6	0.80	1 " 41 "	"	
20	0.00627	"	"	3.75	3.4 " 3.8	3.55	63.5 " 79.5	146.3 " 175.1	0.95	2 " 29 "	"	
21	0.00627	"	"	3.75	3.6 " 3.7	4.06	74.	165.2	1.08	2 " 28 "	"	
22	0.00627	"	"	3.75	2.1 " 2.6	0.5	47. " 85.	116.6 " 185.	0.14	4 " 28 "	No vanadium. Electrolyte yellow-green, blue, emerald-green.	The reduction here went to the state V_2O_3 (sesqui-oxide).
23	0.00627	"	"	3.75	2.53	1.0	74.5 " 81.	166.1 " 177.8	0.28	0 " 55 "	Same.	
24	0.00627	"	"	3.75	2.89 " 3.13	2.0	78. " 82.	172.4 " 179.6	0.56	1 " 59 "	Slight black deposit on cathode. No V. Electrolyte very dark green.	Slight treeing. 22 to 26 saturated with boric acid.
25	0.00627	"	"	3.75	3.41 " 3.9	3.5	56.5 " 76.5	131.9 " 133.7	0.93	2 " 35 "	No vanadium. Electrolyte; reduced to green through blue.	
26	0.00627	"	"	3.75	3.8	4.05	72.	161.6	1.08	2 " 51 "	Same.	
27	0.00627	Mercury	"	6.02	3.2 " 3.65	0.6 to 0.73	46.5 " 81.	115.7 " 177.8	0.10	0 " 55 "	No vanadium. Electrolyte not reduced. Carbon decomposed.	Experiments 27 to 30, inclusive, neutralized. Electrolyte I, with sodium hydroxide, and then saturated with boric acid.
28	0.00627	"	"	6.02	3.6 " 3.65	1.54 " 1.60	84.	183.2	0.26	1 " 3 "	Same.	
29	0.00627	"	"	6.02	4.02 " 4.1	2.58 " 2.6	80.5 " 81.	176.9 " 177.8	0.43	0 " 52 "	"	
30	0.00627	"	"	6.02	4.3 " 4.35	3.52 " 3.56	79. " 80.	174.2 " 176.	0.59	0 " 59 "	"	
31	0.00627	Monel M.	Platinum	2.	2.4	0.25	20. " 24.	68. " 75.2	0.12	4 " 10 "	Dark deposit on cathode. No V. Electrolyte yellow-green-blue.—Resorcine,	Cathode deposits showed tests for copper (31 to 34). Monel M. disintegrated. Also in 31 to 34 used addition agents.
32	0.00627	"	"	2.	2.4	0.25	20. " 24.	68. " 75.2	0.12	4 " 10 "	Same. [Tannic acid, Peptone, Quinoline.	
33	0.00627	"	"	1.5	2.7	0.20	20. " 22.	68. " 71.6	0.12	4 " 5 "	"	
34	0.00627	"	"	1.5	2.65	0.20	20. " 22.	68. " 71.6	0.12	4 " 5 "	"	
34 to 38	Same in every respect as 31 to 34, but weighed cathodes.											
39	0.00627	Platinum	Pt. Wire	3.25	5.4 " 5.	0.5	20.	68.	0.15	1 " 5 "	Cathode no deposit. Electrolyte in cathode compartment reduced to blue-green.	Decrease in weight of cathode.
40	0.00627	"	"	3.25	7.8 " 7.7	1.0	25. " 33.	77. " 91.4	0.30	0 " 27 "		Used a porous cup in which placed cathode.
41	0.00627	"	"	3.25	12.8 " 11.5	2.0	33. " 50.	91.4 " 122.	0.45	0 " 40 "	Same for 40, 41 and 42.	Cathode liquor—Electrolyte I saturated with boric acid. } Saturated with boric acid.
42	0.00627	"	"	3.25	15.0 " 14.0	3.0	50. " 70.	122. " 158.	0.60	0 " 49 "		Anode " 10 c.c. " I + water.

Electrolyte I: 11.35 grams vanadic acid.
27.10 " 26% ammonia.
103.10 " conc. sulphuric acid.
Make up to 2271 c.c. with water.

No.	Concentration V_2O_5 gm./c.c.	Electrodes Cathode	Electrodes Anode	Area of Cathode in sq. in.	Volts	Amps.	Temp. °C.
1	0.00027	Platinum	Carbon	3.7	1.6 to 2.2	0.7	40.0 to 85.
2	0.00027	"	"	2.3	2.5	0.4	82.
3	0.00027	"	"	1.4	1.5	0.4	81.
4	0.00034	"	Platinum	2.5	2.2	0.20	80.
5	0.00034	"	"	2.2	2.7 " 2.75	0.15	70.
6	0.00034	"	"	3.3	2.0	0.05	70.
7	0.00034	"	"	2.2	1.40 " 1.50	0.10	80.
8	0.00037	"	"	3.2	2.70 " 2.9	0.05	80.
9	0.00037	"	"	3.2	3.1 " 3.1	0.08	80.
10	0.00037	"	"	3.2	1.9 " 1.0	0.06	70.
11	0.00037	"	"	2.3	3.6 " 3.2	0.06	80.
12	0.00039	"	"	3.2	1.15	0.07	80.
13	0.00039	"	"	2.2	3.44 " 4.4	0.09	80.
14	0.00039	"	"	2.2	3.7 " 3.2	0.09	70.
15	0.00039	"	"	3.2	3.1 " 3.1	0.07	82.
16	0.00042	Lead	Carbon	3.75	2.0 " 2.7	0.06	84.
17	0.00042	"	"	3.75	2.0 " 2.3	1.07	76.
18	0.00042	"	"	3.75	2.58 " 3.2	2.00	80.
19	0.00042	"	"	3.75	3.0	3.00	75.
20	0.00042	"	"	3.75	2.0 " 1.4	1.05	75.
21	0.00042	"	"	3.75	3.0 " 3.2	4.00	74.
22	0.00042	"	"	3.75	2.1 " 2.0	0.5	80.
23	0.00042	"	"	3.75	2.52	1.0	74.5
24	0.00047	"	"	3.75	2.80 " 3.11	2.0	75.
25	0.00047	"	"	3.75	3.11 " 3.0	1.5	56.5
26	0.00047	"	"	3.75	3.0	1.05	73.
27	0.00047	Nickel	"	6.0	1.2 " 1.05	0.2 to 0.12	1.5 to 91.
28	0.00047	"	"	6.0	1.05 " 1.05	1.34 " 1.00	84.
29	0.00047	"	"	6.0	4.02 " 4.1	2.59 " 2.4	80.5 " 81.
30	0.00047	"	"	6.0	4.1 " 4.15	2.32 " 2.15	79. " 80.
31	0.00047	Chromel M.	Platinum	2	3.4	0.21	80. " 84.
32	0.00047	"	"	2	2.4	0.7	80. " 82.
33	0.00047	"	"	1.5	2.7	0.31	78. " 82.
34	0.00047	"	"	1.5	2.05	0.28	79. " 82.
35	Same in every respect as 31 to 34, but weighed anhydr.						
36	0.00047	Platinum	Pt. Iridium	3.25	2.7 " 2.	0.31	70.
37	0.00047	"	"	3.25	2.3 " 2.	0.	80.
38	0.00047	"	"	3.25	12.2 " 11.2	2.0	80.
39	0.00047	"	"	3.25	15.0 " 14.0	3.0	70.

Electrolyte: 40 c.c. conc. sulphuric acid.
12.09 grams vanadic oxide.
Make up to 2000 c.c. with water.
Part is saturated with aluminium sulphate $Al_2(SO_4)_3.18H_2O$.

TABLE III.

No.	Concentration V_2O_5 gm. c.c.	Electrodes: Cathode	Electrodes: Anode	Area of Cathode in sq. in.	Volts	Amperes	Temperature °C.	Temperature °F.	Current Density per sq. in.	Time	RESULTS	REMARKS
43	0.006	Platinum	Pt. Wire	3.	6.2 to 6.9	1.0	22. to 67.	71.6 to 152.6	0.33	1 hr. 20 min.	No deposits. Added glue. Electrolyte yellow-green to blue to green.	
44	0.006	"	"	3.	10.5 " 9.1	2.0	67. " 70.	152.6 " 158.	0.66	1 " 25 "	Black film on cathode. No V. Added glue. Electrolyte as in 44.	
45	0.006	"	"	3.	11.7 " 13.4	3.0	70. " 91.	158. " 195.8	0.99	1 " 5 "	Same.	
46	0.006	"	"	1.25	3.95 " 4.1	0.25	80. " 84.	176. " 183.2	0.20	1 " 15 "	Cathode showed nothing. Electrolyte yellow-green.	
47	0.006	"	"	1.25	5.6	0.50	75 " 84.	167. " 183.2	0.40	1 " 15 "	" " " " green-blue.	
48	0.006	"	"	1.25	8.8 " 9.4	1.0	75. " 76.	167. " 168.8	0.80	1 " 15 "	" " " " blue-emerald green.	
49	0.006	"	"	1.25	16.	2.0	76.	168.8	1.60	1 " 0 "	" " " " olive green.	
50	0.004	"	"	1.25	4.65 " 4.5	0.25	64. " 66.	147.2 " 150.8	0.2	1 " 15 "	" " " " very dark green.	
51	0.004	"	"	1.25	7.1 " 7.2	0.50	64. " 69.	147.2 " 156.2	0.4	1 " 15 "	Same.	
52	0.004	"	"	1.25	11.9 " 11.2	1.00	69. " 80.	156.2 " 176.	0.8	1 " 15 "	"	Experiments 46 to 57. To the vanadic sulphate solution only 10 gm. of aluminium sulphate were added.
53	0.004	"	"	1.25	20.3 " 21.3	2.00	80. " 94.	176. " 201.2	1.6	1 " 0 "	"	
54	0.002	"	"	1.25	5.4 " 5.6	0.25	66.	150.8	0.2	1 " 15 "	"	
55	0.002	"	"	1.25	9.0 " 9.5	0.50	66. " 67.	150.8 " 152.6	0.4	1 " 15 "	"	
56	0.002	"	"	1.25	16.	1.00	67. " 80.	152.6 " 176.	0.8	1 " 15 "	"	
57	0.002	"	"	1.25	32.	2.00	80. " 98.	176. " 208.4	1.6	1 " 0 "	"	
58	0.006	"	"	2.25	11.4 " 6.6	0.5 to 0.75	19.5 " 58.5	67.1 " 137.3	0.22 to 0.33	3 " 5 "	No deposits. Electrolyte reduced.	Used porous cell in 58, 59 and 60. Anode liquor vanadic sulphate solution (10 c.c.) + water and cathode liquor, vanadic sulphate solution + aluminium sulphate (saturated).
59	0.006	"	"	2.25	10.4	1.5 " 1.68	58.5 " 69.	137.3 " 156.2	0.67 " 0.76	2 " 0 "	Cathode deposits, film, brown-black. Electrolyte reduced to lavender.	
60	0.006	"	"	2.25	12.8 " 8.7	2.00	69. " 70.5	156.2 " 158.9	0.89	2 " 0 "	Same. Final electrolyte lavender to gray. No. V.	
61	0.006	"	"	1.5	7.0	0.25	21. " 24.	69.8 " 75.2	0.17	1 " 10 "	No deposition. Electrolyte yellow-green-blue.	
62	0.006	"	"	1.5	7.1 " 6.1	0.3 " 0.375	26. " 55.	78.8 " 131.	0.2 " 0.25	1 " 10 "	Same.	
63	0.006	"	"	1.5	13. " 4.2	1.0	84. " 74.	183.2 " 165.2	0.67	1 " 5 "	"	
64	0.006	"	"	1.5	6. " 5.3	2.0	97. " 100.	206.6 " 212.	1.34	1 " 15 "	Black film. Electrolyte green to lavender.	Cathode liquor—vanadic sulphate solution + sat. $Al_2(SO_4)_3.18H_2O$. 61 to 65. Used porous cell. Anode liquor: H_2SO_4 + water. Cathode liquor diffused readily through porous cell. Black film: platinum hydride. Cell gave 0.1 volts.
65	0.006	"	"	1.5	7.5 " 7.3	3.0	101.	213.8	2.01	1 " 0 "	" " " " " " (muddy).	

Electrolyte: 40 c.c. conc. sulphuric acid.
12.19 grams vanadic oxide.
Made up to 2000 c.c. with water.
Part of this is saturated with magnesium sulphate $MgSO_4.7H_2O$.

TABLE IV.

66	0.006	Platinum	Pt. Wire	3.	5.3 to 5.45	1.0	17. to 47.	62.6 to 116.6	0.33	1 hr. 20 min.	No deposits. Electrolyte yellow-green-blue.	
67	0.006	"	"	3.	7.9 " 8.2	2.0	47. " 66.5	116.6 " 151.7	0.66	1 " 25 "	Cathode, brown-black film. Electrolyte blue at end.	
68	0.006	"	"	3.	10.3 " 9.35	3.0	66.5 " 76.	151.7 " 168.8	0.99	1 " 5 "	Same.	
69	0.006	"	"	1.25	13.3 " 3.4	0.25	20. " 54.	68. " 129.2	0.20	1 " 15 "	No deposits. Electrolyte yellow-green.	
70	0.006	"	"	1.25	4.3 " 4.5	0.3 to 0.375	54. " 77.	129.2 " 170.6	0.40	1 " 15 "	" " " green-blue.	
71	0.006	"	"	1.25	6.1 " 6.9	1.0	77. " 78.	170.6 " 172.4	0.80	1 " 15 "	" " " blue.	
72	0.006	"	"	1.25	10.5 " 12.0	2.0	78.	172.4	1.60	1 " 0 "	" " " blue-green.	
73	0.004	"	"	1.25	3.75 " 6.35	0.25	63. " 67.	145.4 " 152.6	0.20	1 " 15 "	" " Green.	
74	0.004	"	"	1.25	5.4 " 5.7	0.50	67. " 71.	152.6 " 159.8	0.40	1 " 15 "	" " "	
75	0.004	"	"	1.25	9.2 " 8.3	1.00	71. " 77.	159.8 " 170.6	0.80	1 " 15 "	" " "	Experiments 69 to 80: Add 20 gm. of magnesium sulphate to the vanadic sulphate solution.
76	0.004	"	"	1.25	13.8 " 13.2	2.00	77. " 85.	170.6 " 185.	1.60	1 " 0 "	" " "	
77	0.003	"	"	1.25	4.3	0.25	69.	156.2	0.20	1 " 15 "	" " "	
78	0.003	"	"	1.25	6.6 " 7.7	0.50	68.	154.4	0.40	1 " 15 "	" " "	
79	0.003	"	"	1.25	11.3 " 10.0	1.00	68. " 78.	154.4 " 172.4	0.80	1 " 15 "	" " "	
80	0.003	"	"	1.25	31.	2.00	78.	172.4	1.60	1 " 0 "	" " "	
81	0.006	"	"	2.25	13. " 6.8	0.5 " 0.75	19.5 " 51.5	67.1 " 124.7	0.22 " 0.33	3 " 5 "	Light film on cathode, black. Electrolyte yellow-blue.	
82	0.006	"	"	2.25	92.	1.5 " 1.68	51.5 " 61.	124.7 " 141.8	0.67 " 0.76	2 " 0 "	Deposit on cathode brown mixed with white. Electrolyte yellow to blue.	Use porous cell. Magnesium-vanadium salt in cell. Outside: Anode liquor, water and sulphuric acid.
83	0.006	"	"	2.25	10.5 " 84.	2.0	61. " 63.5	141.8 " 146.3	0.89	2 " 0 "	Same.	
84	0.006	"	"	1.50	12.0 " 10.5	0.25	23. " 25.	73.4 " 77.	0.17	1 " 10 "	No deposits. Electrolyte deduced.	
85	0.006	"	"	1.50	9.8 " 7.7	0.3 " 0.375	28. " 63.	82.4 " 145.4	0.2 " 0.25	1 " 10 "	" " " " to blue.	Used porous cell again.
86	0.006	"	"	1.50	14.0 " 6.8	1.0	88. " 84.	190.4 " 183.2	0.67	1 " 5 "	" "	Electrolyte diffused readily through cell.
87	0.006	"	"	1.50	8.9 " 6.6	2.0	84. " 96.	183.2 " 204.8	1.34	1 " 15 "	Brownish coating on cathode. Electrolyte green.	
88	0.006	"	"	1.50	8.0 " 7.9	3.0	97.	206.6	2.01	1 " 0 "	" " (olive green—green).	Deposits: Brownish grey contained V_2O_5: 25.46%. Mg: 24.88.

Electrolyte: 40 c.c. conc. sulphuric acid
12.09 grams vanadic oxide
Made up to 2000 c.c. with water.
Part is saturated with aluminum sulphate $Al_2(SO_4)_3 \cdot 18H_2O$

No.	Concentration Vanadic oxide	Electrodes Cathode	Electrodes Anode	Area of Cathode in sq. m.	Volts	Amperes	Temp. °C.
1	0.005	Platinum	Pt. Wire	3.	9.2 to 6.9	1.0	22. to 0.
2	0.005	"	"	3.	10.5 " 9.1	2.0	0. " 70.
3	0.005	"	"	3.	11.7 " 11.4	3.0	70. " 0.
4	0.005	"	"	1.25	7.95 " 4.1	0.25	0. " 64.
5	0.005	"	"	1.25	8.0	0.50	75. " 0.
6	0.005	"	"	1.25	8.3 " 9.4	1.0	72. " 0.
7	0.005	"	"	1.25	10.	2.0	70.
8	0.004	"	"	1.25	4.5 " 4.5	0.25	74. " 0.
9	0.004	"	"	1.25	5.0 " 7.2	0.50	71. " 0.
10	0.004	"	"	1.25	11.5 " 11.2	1.00	68. " 0.
11	0.004	"	"	1.25	12.5 " 21.3	2.00	60. " 0.
12	0.002	"	"	1.25	4.0 " 4.6	0.25	65.
13	0.002	"	"	1.25	5.0 " 9.5	0.50	65. " 0.
14	0.002	"	"	1.25	10.	1.00	62. " 0.
15	0.002	"	"	1.25	15.	2.00	60. " 0.
16	0.006	"	"	2.25	11.4 " 6.0	0.5 to 0.25	0.75 " 0.
17	0.006	"	"	2.25	14.4	1.5 " 1.0	58.5 " 0.
18	0.006	"	"	2.25	12.8 " 8.7	2.00	0. " 0.
19	0.006	"	"	2.5	7.0	0.25	0. " 0.
20	0.005	"	"	1.5	10. " 6.1	0.3 " 0.275	0. " 0.
23	0.005	"	"	1.5	11. " 4.3	1.0	34. " 0.
24	0.006	"	"	1.5	6. " 5.5	2.0	0. " 0.
25	0.005	"	"	1.5	7.5 " 7.5	3.0	100.

Electrolyte: 40 c.c. conc. sulphuric acid
12.09 grams vanadic oxide
Made up to 2000 c.c. with water.
Part of this is saturated with magnesium sulphate $MgSO_4 \cdot 7H_2O$

No.	Concentration Vanadic oxide	Electrodes Cathode	Electrodes Anode	Area of Cathode in sq. m.	Volts	Amperes	Temp. °C.
26	0.005	Platinum	Pt. Wire	2.	5.5 to 5.45	1.0	17. " 0.
27	0.005	"	"	3.	7.0 " 8.2	2.0	0. " 0.
28	0.005	"	"	3.	10.0 " 13.5	3.0	0. " 0.
29	0.005	"	"	1.25	15.0 " 3.1	0.25	0. " 0.
30	0.005	"	"	1.25	8.8 " 4.5	0.5 to 0.475	0. " 0.
31	0.005	"	"	1.25	9.0 " 6.5	1.0	0. " 0.
32	0.005	"	"	1.25	10.5 " 12.5	2.0	0.
33	0.004	"	"	1.25	5.75 " 5.1	0.25	0. " 0.
34	0.004	"	"	1.25	8.8 " 5.0	0.50	0. " 0.
35	0.004	"	"	1.25	9.2 " 8.0	1.0	0. " 0.
36	0.004	"	"	1.25	12.8 " 15.5	2.0	0. " 0.
37	0.003	"	"	1.25	4.5	0.25	0.
38	0.003	"	"	1.25	6.0 " 7.7	0.50	0.
39	0.003	"	"	1.25	11.0 " 10.0	1.00	0. " 0.
40	0.003	"	"	1.25	17.	2.00	0.
41	0.006	"	"	2.25	11. " 6.0	0.5 to 0.25	0. " 0.
42	0.006	"	"	2.25	12.	1.5	0. " 0.
43	0.006	"	"	2.25	17.5 " 8.0	2.0	0. " 0.
44	0.006	"	"	1.50	12.0 " 10.5	0.25	0. " 0.
45	0.006	"	"	1.50	9.5 " 7.1	0.2 " 0.195	0. " 0.
46	0.006	"	"	1.50	14.0 " 6.3	1.0	0. " 0.
47	0.006	"	"	1.50	8.0 " 6.0	2.0	0. " 0.
48	0.006	"	"	1.50	8.0 " 7.5	3.0	0.

TABLE V.

Electrolyte.
100 c.c. hydrofluoric acid (48% HF).
21 grams boric acid.
Make up to 400 c.c.
Take 50 c.c. add 1.4984 gm. V. acid.
Make up to 300 c.c.

No.	Concentration V_2O_5 gm. c.c.	Electrodes Cathode	Electrodes Anode	Area of Cathode in sq. in.	Volts	Amperes	Temperature °C.	Temperature °F.	Current Density per sq. in.	Time	RESULTS	REMARKS
89	0.02997	Platinum	Carbon	1.5	2. to 2.52	0.45 to 0.5	21. to 45.	69.8 to 113.	0.3 to 0.33	0 hr. 50 min.	Nothing.	
90	0.02997	"	"	1.5	3. " 2.80	1.5	45. " 57.	113. " 134.6	1.00	0 " 40 "	"	100 c.c. of fluoboric acid as made + 2.997 gm. V_2O_5, for 89 to 93.
91	0.02997	"	"	1.5	3.4 " 3.9	2.5	57. " 49.	134.6 " 120.2	1.67	0 " 40 "	Black film on cathode. Electrolyte greenish-yellow-green.	Carbon anode disintegrated.
92	0.02997	"	"	1.5	4.3 " 4.5	3.5	49. " 51.	120.2 " 123.8	2.33	0 " 35 "	Same.	
93	0.02997	"	"	1.5	4.7 " 5.4	4.5	51.	123.8	3.00	1 " 5 "	"	
94	0.005	Monel M.	"	3.0	3.3 " 3.4	0.5 " 0.6	18. " 44.	64.4 " 111.2	0.17 " 0.20	3 " 0 "	Cathode showed fine black film. Electrolyte emerald to blue.	Cathode disintegrated.
95	0.005	"	"	3.0	1.7 " 2.8	0.25	20. " 46.	68. " 114.8	0.08	5 " 1 "	Same.	
96	0.005	Platinum	Pt. Wire	1.5	3.9 " 5.5	1.03	20. " 49.	68. " 120.2	0.69	4 " 0 "	No deposition. Electrolyte from green to blue.	
97	0.005	Monel M.	"	2.25	6.5 " 5.8	1.8 " 1.95	20. " 44.	68. " 111.2	0.8 " 0.87	4 " 10 "	" " " " green to blue.	
98	0.005	Platinum	"	1.5	2.6 " 2.95	0.25	19.5 " 30.	67.1 " 86.	0.17	0 " 55 "	Nothing. " " green to blue.	Used porous partition (fish skin). Was easily attacked and useless.
99	0.005	"	"	1.5	4.3 " 4.4	0.54 " 0.55	31.	87.8	0.36 " 0.37	1 " 29 "	Black coating. " " green to blue.	Deposit on cathode platinum hydride.
100	0.005	"	"	1.5	6.0 " 6.2	1.00	31. " 34.	87.8 " 93.2	0.67	0 " 55 "	Same.	
101	0.005	"	"	1.5	9.6 " 9.1	2.00	34.	93.2	1.34	0. " 40 "	"	

TABLE VI.

Electrolyte.
100 c.c. hydrofluoric acid (48% HF).
24.1 gm. silica SiO_2.
Make up to 400 c.c.
Take 50 c.c. add 0.6224 gm. V. acid.
Make up to 400 c.c.

No.	Concentration V_2O_5 gm. c.c.	Electrodes Cathode	Electrodes Anode	Area of Cathode in sq. in.	Volts	Amperes	Temperature °C.	Temperature °F.	Current Density per sq. in.	Time	RESULTS	REMARKS
102	0.01245	Platinum	Carbon	1.5	1.6 to 2.63	0.45 to 0.5	21. to 45.	69.8 to 113.	0.3 to 0.33	0 hr. 50 min.	Nothing.	100 c.c. of fluosilicic acid as prepared, saturated with 1.2448 gm. vanadic acid. Used for 102-106 inclusive.
103	0.01245	"	"	1.5	3.2 " 3.00	1.5	45. " 54.	113. " 129.2	1.0	0 " 40 "	Black film on cathode.	
104	0.01245	"	"	1.5	3.8 " 4.10	2.5	54. " 59.	129.2 " 138.2	1.67	0 " 40 "	Same.	Black deposit proved to be platinum hydride.
105	0.01245	"	"	1.5	4.7 " 4.3	3.5	59. " 64.	138.2 " 147.2	2.33	0 " 35 "	" Electrolyte from green to blue.	
106	0.01245	"	"	1.5	5.15 " 5.7	4.5	64. " 66.	147.2 " 150.8	3.00	1 " 5 "	"	
107	0.00307	Monel M.	"	2.75	3.35 " 3.1	0.5 " 0.6	18. " 45.	64.4 " 113.	0.19	3 " 0 "	Cathode; black film. Electrolyte reduced from light green to blue.	
108	0.00307	"	"	2.75	1.60 " 2.7	0.25	20. " 47.	68. " 116.6	0.09	5 " 1 "	" " " easily rubbed off and grayish underneath. Electrolyte same.	
109	0.00307	Platinum	Pt. Wire	2.75	4.50 " 3.8	1.10	20. " 45.	68. " 113.	0.40	4 " 0 "	" " " underneath; yellowish tinge. No. V. Electrolyte green.	
110	0.00307	Monel M.	"	2.25	6.9 " 6.6	1.8 " 1.95	20. " 45.	68. " 113.	0.8 " 0.87	4 " 10 "	Nothing. Electrolyte green to blue.	
111	0.00307	Platinum	"	1.5	2.4 " 4.8	0.25	20. " 30.	68. " 86.	0.17	0 " 55 "	" " " " "	Used fish skin as partition.
112	0.00307	"	"	1.5	3.25 " 3.4	0.54 " 0.55	30. " 45.	86. " 113.	0.36 " 0.37	1 " 29 "	" " " " "	Partition destroyed by acid. Useless.

TABLE VII. ACIDS.

Electrolyte I: 500 c.c. conc. Hydrochloric Acid (36.5 %).
66.5 grams Vanadic Acid (99.376 pure).

No.	Concentration V_2O_5 gm. c.c.	Electrodes Cathode	Electrodes Anode	Area of Cathode in sq. in.	Volts	Amperes	Temperature °C.	Temperature °F.	Current Density per sq. in.	Time	RESULTS	REMARKS
1	0.133	Platinum	Carbon	0.750	1.9 to 1.3	0.25	22 to 96	71.6 to 204.8	0.33	1 hr. 10 min.	Nothing. Electrolyte from dark blue to light blue.	C. E. M. F. 0.025 V.
2	0.133	"	"	1.125	1.5 " 1.2	0.25	22 " 98	71.6 " 208.4	0.22	1 " 10 "	Same.	C. E. M. F. 0.025 V.
3	0.133	"	"	1.500	1.75 " 1.2	0.25	22 " 100	71.6 " 212	0.17	1 " 10 "	"	C. E. M. F. 0.05 V.
4	0.133	Lead	"	0.750	1.95 " 1.7	0.25	22 " 96	71.6 " 204.8	0.33	1 " 10 "	"	+ E. M. F. 0.10 V.
5	0.133	"	"	1.125	1.95 " 1.65	0.25	22 " 104	71.6 " 219.2	0.22	1 " 10 "	"	+ E. M. F. 0.10 V. Lead formed $PbCl_2$, lead chloride. Pb as cathode.
6	0.133	"	"	1.500	1.90 " 1.70	0.25	22 " 99	71.6 " 210.2	0.17	1 " 10 "	"	+ E. M. F. 0.10 V. Useless.
7	0.034	"	"	0.750	2.35 " 1.70	0.25	25 " 99	77 " 210.2	0.33	1 " 10 "	Dark film on cathode. No V. Electrolyte green-blue, blue-green.	+ E. M. F. 0.10 V.
8	0.034	"	"	0.125	2.30 " 1.60	0.25	23 " 100	73.4 " 212	0.22	1 " 10 "	Same.	+ E. M. F. 0.10 V.
9	0.034	"	"	0.150	2.10 " 1.50	0.25	22 " 97	71.6 " 206.6	0.17	1 " 10 "	"	+ E. M. F. 0.10 V.
10	0.133	Platinum	Pt. Wire	0.750	1.2 " 1.4	0.25	22 " 24	71.6 " 75.2	0.33	0 " 35 "	Nothing. Electrolyte dark blue at start.	
11	0.133	"	"	0.750	1.65 " 1.3	0.50	24 " 64	75.2 " 147.2	0.66	0 " 30 "	Nothing on cathode. Electrolyte dark blue to dark green.	
12	0.133	"	"	0.750	1.5 " 1.3	1.00	64 " 89	147.2 " 192.2	1.32	0 " 30 "	Same.	
13	0.133	"	"	0.750	1.8 " 1.85	2.00	89 " 103	192.2 " 217.4	2.64	0 " 30 "	Black film on cathode. Trace V. Electrolyte dark green.	
14	0.133	"	Carbon	1.125	1.6	0.25	21 " 24	69.8 " 75.2	0.22	0 " 35 "	Nothing.	V. trace due to occluded electrolyte. Deposit was Pt—hydride.
15	0.133	"	"	1.125	2.0 " 1.4	0.50	24 " 74	75.2 " 165.2	0.44	0 " 30 "	"	Experiments 14 to 17 incl. used porous cell.
16	0.133	"	"	1.125	1.9 " 2.0	1.00	73 " 63	163.4 " 145.4	0.88	0 " 30 "	Dark film on cathode. Cathode liquor blue. No V on cathode.	Cathode liquor conc. HCl + vanadic acid.
17	0.133	"	"	1.125	2.8	2.00	63	145.4	1.76	0 " 30 "	Same.	Anode liquor water + few drops hydrochloric acid.
18	0.133	"	"	0.75	2.3 " 1.69	1.00	21 " 74	69.8 " 165.2	1.32	6 " 30 "	Gray film on cathode. Cathode liquor light green. Anode L. blue-green.	Porous cup. In porous cup water + HCl. Outside conc. HCl + V. acid.
19	0.133	"	"	0.94	2.85 " 1.9	1.00	21 " 76	69.8 " 168.8	1.06	6 " 30 "	Same on cathode. Cathode liquor dark green, green, blue.	Porous cup. In porous cup conc. HCl + V_2O_5. Outside H_2O + HCl.
20	0.133	"	"	1.31	9.3 " 2.8	1.00	33 " 52	91.4 " 125.6	0.76	6 " 30 "	Exactly same as No. 19.	Run similarly to No. 13.
21	0.133	"	"	1.00	2.64 " 1.78	1.00	30 " 34	86 " 93.2	1.00	3 " 25 "	Same as Exp. 18.	Same as Exp. 18. Change in current density.
22	0.133	"	"	0.75	2.4 " 2.98	1.00	30 " 33	86 " 91.4	1.32	3 " 25 "	" " " " Conducted to test for vanadic acid	
23	0.133	"	"	0.50	2.6 " 2.94	1.00	30 " 36	86 " 96.8	2.00	3 " 25 "	" " " " on anode. None found.	
24	0.133	"	"	0.25	2.8 " 2.7	1.00	29 " 39	84.2 " 102.2	4.00	3 " 25 "	" " " "	
25	0.133	"	"	1.50	1.34 " 1.65	1.00	68 " 95	154.4 " 203	0.67	2 " 10 "	Black film on cathode. Electrolyte green-blue-green.	25, 26 27 made to test black deposit. Increased weight cath. 0.0003 gm.
26	0.133	"	"	1.13	1.48 " 1.73	1.00	81 " 92	177.8 " 197.6	0.89	2 " 10 "	Same.	Conductivity uniform all over. " " " 0.0008 gm.
27	0.133	"	"	0.75	1.47 " 1.63	1.00	73 " 87	163.4 " 188.6	1.33	2 " 10 "	"	Cathode with deposit. " " " 0.0020 gm.

[illegible] c.c. Hydrocyanic Acid (0.5 HCN).
[illegible] grams Vinegar Acid (99.5% pure).
Make up to [illegible] c.c.

Electrodes
[illegible] c.c. and 1 [illegible] cm. V. acid.
Make up to [illegible] c.c.

No.	Concentration V.A. grams per c.c.	Electrodes: Cathode	Electrodes: Anode	Area of Cathode in sq. cm.	Volts	Time in minutes	Time in minutes	Time in minutes
1	0.0250	Platinum	Carbon	1.5	2.2	0.5	25	45
2	0.0250	"	"	1.5	2.4	1	25	7
3	0.0250	"	"	1.5	2.6	2	25	10
4	0.0250	"	"	1.5	2.3	3	25	15
5	0.0250	"	"	1.5	2.4	5	25	20
6	0.05	Platinum	Carbon	3.1	3.4	0.5	15	25
7	0.05	"	"	3.0	2.7	0.5	20	30
8	0.05	Platinum	Pt. Wire	1.5	2.9	1.0	20	40
9	0.05	Mond Ni.	"	2.25	3.2	0.5	20	35
10	0.05	Platinum	"	1.5	2.9	0.5	20	35
11	0.05	"	"	1.5	4.4	0.5	21	35
12	0.05	"	"	1.5	2.7	1.0	21	35
13	0.05	"	"	1.5	2.1	0.0	24	40

Electrolyte
Take 50 c.c. and 0.[illegible] c.c. V. acid.
Make up to 400 c.c.

No.	Concentration V.A. grams per c.c.	Electrodes: Cathode	Electrodes: Anode	Area of Cathode in sq. cm.	Volts	Time in minutes	Time in minutes	Time in minutes
102	0.0125	Platinum	Carbon	1.5	[illegible]	[illegible]	[illegible]	[illegible]
103	0.0125	"	"	1.5	3.2	1.0	17	7
104	0.0125	"	"	1.5	3.5	1.0	17	10
105	0.0125	"	"	1.5	4.0	2	17	15
106	0.0125	"	"	1.5	4.1	3	5	20
107	0.0125	"	"	1.5	3.2	4.5	17	20
108	0.0125	Mond Ni.	"	2.25	3.1	0.5	15	25
109	0.0125	"	"	2.25	3.0	1.0	21	35
110	0.0125	Platinum	Pt. Wire	2.25	4.50	1.0	20	30
111	0.0125	Mond Ni.	"	2.25	3.0	1.0	20	45
112	0.0125	Platinum	"	1.5	3.8	1.0	21	30
113	0.0125	"	"	1.5	3.3	1.0	30	45

Electrolyte 1: 200 c.c. conc. Hydrochloric Acid (36.5 %).
[illegible] grams Vinegar Acid (99.5% pure).

No.	Concentration V.A. grams per c.c.	Electrodes: Cathode	Electrodes: Anode	Area of Cathode in sq. cm.	Volts	Time in minutes	Time in minutes	Time in minutes
1	0.125	Platinum	Carbon	0.750	1.0	0.5	22	30
2	0.125	"	"	1.125	1.2	0.5	22	30
3	0.125	"	"	1.500	1.25	0.5	22	40
4	0.125	Lead	"	0.750	1.25	0.5	22	25
5	0.125	"	"	1.125	1.30	0.5	22	30
6	0.133	"	"	1.500	1.00	0.50	22	25
7	0.083	"	"	0.750	1.05	0.50	22	30
8	0.064	"	"	0.125	1.30	0.50	22	100
9	0.064	"	"	0.150	2.10	1.50	22	90
10	0.133	Platinum	Pt. Wire	0.750	1.2	0.25	22	20
11	0.133	"	"	0.750	1.05	0.50	24	30
12	0.133	"	"	0.750	1.5	1.50	24	45
13	0.133	"	"	0.750	1.8	1.50	60	100
14	0.133	"	Carbon	1.125	1.5	0.25	21	90
15	0.133	"	"	1.125	2.0	1.4	21	24
16	0.133	"	"	1.125	2.0	0.50	21	30
17	0.133	"	"	1.125	2.0	1.00	21	30
18	0.125	"	"	0.75	1.0	1.00	21	24
19	0.125	"	"	0.94	1.0	1.00	21	30
20	0.133	"	"	1.01	1.0	1.00	21	30
21	0.133	"	"	1.00	1.0	1.00	21	30
22	0.133	"	"	0.75	2.4	1.00	21	30
23	0.133	"	"	0.50	2.5	1.00	21	30
24	0.133	"	"	0.25	2.8	1.00	21	30
25	0.133	"	"	1.50	1.34	1.00	21	30
26	0.133	"	"	1.10	1.48	1.00	21	30
27	0.133	"	"	0.75	1.47	1.00	21	30

Electrolyte II a. 12.19 grams Vanadic Acid.
40 c.c. conc. Sulphuric Acid.
Made up to 2000 c.c.

TABLE VIII.

No.	Concentration V_2O_5 gm. c.c.	Electrodes: Cathode	Electrodes: Anode	Area of Cathode in sq. in.	Volts	Amperes	Temperature °C.	Temperature °F.	Current Density per sq. in.	Time	RESULTS	REMARKS
28	0.006	Platinum	Pt. Wire	1.5	2.5 to 2.7	0.25	18 to 42	64.4 to 107.6	0.17	1 hr. 15 min.	No deposit. Electrolyte yellow-green-blue.	
29	0.006	"	"	1.5	2.9 " 3.0	0.50	42 " 61	107.6 " 141.8	0.34	1 " 15 "	Same.	
30	0.006	"	"	1.5	3.9 " 3.8	1.00	61 " 75	141.8 " 167	0.68	1 " 15 "	"	
31	0.006	"	"	1.5	5.3 " 5.7	2.00	75 " 90	167 " 194	1.36	1 " 15 "	"	
32	0.003	"	"	1.5	2.0 " 3.2	0.25	49 " 53	120.2 " 127.4	0.17	1 " 15 "	"	
33	0.003	"	"	1.5	4.0 " 3.8	0.50	71 " 72	159.8 " 161.6	0.34	1 " 15 "	"	
34	0.003	"	"	1.5	5.4 " 5.6	1.00	72 " 82	161.6 " 179.6	0.68	1 " 15 "	"	
35	0.003	"	"	1.5	8.6 " 8.3	2.00	82 " 86	179.6 " 186.8	1.36	1 " 15 "	"	
36	0.0015	"	"	1.5	4.2 " 3.9	0.25	61 " 85	141.8 " 185	0.17	1 " 15 "	"	
37	0.0015	"	"	1.5	5.7 " 5.6	0.50	85 " 92	185 " 197.6	0.34	1 " 15 "	"	In Exp. 40 to 46 vanadic acid was dissolved in conc. sulphuric acid to saturation, i. e., 0.304 gm. vanadic acid per 1 c.c. sulphuric acid.
38	0.0015	"	"	1.5	9.1 " 9.2	1.00	92	197.6	0.68	1 " 15 "	"	The deposit is green. It is readily soluble in alcohol, water and in ether containing sulphuric acid (esther). In water the salt changes over to the vanadyl salt (blue).
39	0.0015	"	"	1.5	16.0 " 15.0	2.00	92	197.6	1.36	1 " 15 "	"	The efficiency could not be obtained, as the salt was soluble in the mentioned liquids. On drying from alcoholic solution, salt turned blue.
40	0.304	"	"	3.0	3.4 " 3.1	0.25	19 " 90	66.2 " 194	0.08	1 " 15 "	Green crust on cathode; thin. Electrolyte green.	Salt very unstable, going over into the vanadyl form from the original sesqui-oxide state. Deposit: Green-sulphate of V_2O_3; blue of V_2O_4.
41	0.304	"	"	3.0	3.1 " 3.45	1.00	90 " 110	194 " 230	0.33	3 " 12 "	" " " " heavy. " "	
42	0.304	"	"	3.0	3.6 " 3.8	2.00	110 " 120	230 " 248	0.66	1 " 5 "	Same.	
43	0.304	"	"	1.63	2.8 " 3.1	0.50	103 " 105	217.4 " 221	0.31	1 " 0 "	"	
44	0.304	"	"	1.63	7.2 " 3.4	1.00	19 " 91	66.2 " 195.8	0.62	0 " 50 "	" Deposit adhered to cathode firmly.	
45	0.304	"	"	1.63	3.95 " 4.5	1.50	94 " 113	201.2 " 235.4	0.93	0 " 58 "	" but the green salt deposited directly from the electrolyte.	
46	0.304	"	"	1.63	5.70 " 5.15	2.00	61 " 101	141.8 " 213.8	1.24	2 " 30 "	Same as 55.	
47	0.02	"	"	1.50	3.95 " 4.5	1.00	23 " 38	73.4 " 100.4	0.67	3 " 0 "	Green deposit on cathode. Electrolyte green and clear.	
48	0.02	"	"	0.76	4.8 " 5.95	1.00	27 " 55	80.6 " 131	1.34	3 " 0 "	" " " " Salt precipitated from electrolyte.	Same unstable sulphate as in Exp. 40 to 46.
49	0.02	"	Carbon	Did not work due to carbon anode disintegrating so rapidly that in very short time current was broken.								
50	0.02	"	"									
51	0.02	Lead	"									
52	0.02	"	"	Same.								
53	0.02	Platinum	"	1.5	3.2 to 3.65	0.625	35 to 53	95 to 127.4	0.42	1 hr. 5 min.	No deposit. Electrolyte from yellow to green.	
54	0.02	"	"	1.5	4.3 " 4.10	1.000	36 " 38	96.8 " 100.4	0.67	1 " 22 "	No deposit on cathode. Elec. green. Small amt. gr. precip. bottom cup.	
55	0.02	"	"	1.31	3.35 " 3.8	0.625	34 " 44	93.2 " 111.2	0.48	1 " 5 "	No deposit. Electrolyte yellow-green.	
56	0.02	"	"	1.31	4.4 " 4.7	1.00	38 " 40	100.4 " 104	0.76	1 " 22 "	No deposit. Elec. green. At bottom of cup some of green precipitate.	54 to 64 porous cup used.
57	0.02	"	"	0.75	3.5 " 4.15	0.625	35 " 43	95 " 109.4	0.83	1 " 5 "	No deposit. Electrolyte green.	54 to 64 acted very much slower than 40 to 46, but similarly.
58	0.02	"	"	0.75	5.1 " 4.85	1.000	35 " 41	95 " 105.8	1.33	1 " 22 "	No deposit. Elec. green. At bottom of cup some of green precipitate.	When carbon anodes were used, 49 to 58, the carbon electrodes disintegrated.
59	0.02	"	Lead	1.5	4.9 " 4.75	1.00	24 " 27	75.2 " 80.6	0.67	1 " 30 "	Nothing. Electrolyte did not conduct current long enough.	Lead anodes gradually formed $PbSO_4$ on the surface, and then the current stopped flowing.
60	0.02	"	"	1.31	6.8 " 4.75	1.00	24 " 27	75.2 " 80.6	0.76	1 " 30 "	Same.	
61	0.02	"	"	0.75	6.5 " 3.25	1.00	44 " 77	111.2 " 170.6	1.33	1 " 30 "	"	
62	0.02	"	Pt. Wire	1.5	5.5 " 4.85	1.00	25 " 33	77 " 91.4	0.67	1 " 30 "	Same as 54.	Experiments 62 to 72 were run as checks on 54, 56 and 58.
63	0.02	"	"	1.31	6.5 " 6.00	1.00	26 " 32	78.8 " 89.6	0.76	1 " 30 "	Same as 56.	
64	0.02	"	"	0.75	5.15 " 4.7	1.00	34 " 37	93.2 " 98.6	1.33	1 " 30 "	Same as 58.	

Vanadic acid in conc. nitric acid. This did not work, as 100 c.c. of the nitric acid only dissolved less than 0.5 gm. V_2O_5.
1 : 1 Nitric : water; showed no difference
1 : 2 " : " " " "
1 : 3 " : " " " "
1 : 4 " : " " " "
1 : 5 " : " " " "
So little vanadic acid going into solution the investigation is unnecessary.

Electrolyte IV: 100 c.c. hydrofluoric acid (48%) made up to 400 c.c.
50 c.c. of this electrolyte saturated with 4.8657 gm. vanadic acid. Made up to 300 c.c.

TABLE IX.

65	0.016	Monel	Carbon	3.00	2.75 to 3.4	0.50	23 to 50	73.4 to 122	0.17	2 hr. 30 min.	Black deposit on cathode. No vanadium. Electrolyte green to blue.	Monel metal disintegrated.
66	0.016	Platinum	"	3.00	3.05 " 2.4	0.25	20 " 49	68 " 120.2	0.08	3 " 25 "	Nothing. Electrolyte blue-green at end.	

Electrolyte V. { 20 cc. conc. lactic acid; 10.13 gm. mandic acid; Make up to 500 cc. with water. } Dissolve

No.	Concentration Vols. gm. cc.	Electrodes: Cathode	Electrodes: Anode	Area of Cathode in sq. cm.	Volts	Amperes	Temperature °C
67	0.032	Platinum	Platinum	1.25	7.5 to 11	0.22	18 to 26
68	0.032	"	"	1.25	21 " 25	0.20	20 " 25
69	0.012	"	"	1.25	15.5 " 20.5	0.25	20 " 25
70	0.032	"	"	1.25	5 " 22	1.00	20 " 25
71	0.012	"	"	1.25	40 " 55	2.00	20 " 25
72	0.016	"	"	1.25	62 " 355	0.25	20 " 25
73	0.016	"	"	1.25	64 " 100	0.30	20 " 25
74	0.016	"	"	1.25	75.5 " 295	[illegible]	20 " 25
75	0.008	"	"	1.25	52 " 90	[illegible]	[illegible]
76	0.008	"	"	1.25	65 " 100	0.35	20 " 25
77	0.008	"	"	1.25	110 " 124	1.10	20 " 25
78	0.004	"	"	1.25	64 " 76	0.05	20 " 25
79	0.004	"	"	1.25	91 " 95	0.10	20 " 25
80	0.002	"	"	1.25	94 " 72	0.01	20 " 25
81	0.002	"	"	1.25	117	0.01	20 " 25
Lactic acid (conc.) saturated with mandic acid, dilute one quarter in water							
82	0.02	Platinum	Pt. Wire	1.5	44 to 54	0.15	20 to 25
83	0.02	"	"	1.5	47	0.30	20 " 25
84	0.02	"	"	1.5	53 " 60	1.00	20 " 25

Electrolyte VI. 20 cc. of Ethyl-sulphuric acid is saturated with hippuric mandic acid. Dilute

No.	Concentration Vols. gm. cc.	Electrodes: Cathode	Electrodes: Anode	Area of Cathode in sq. cm.	Volts	Amperes	Temperature °C
85	0.02	Platinum	Platinum	1.25	2.0 to 2.7	0.07	18 to 25
86	0.02	"	"	1.25	2.0 " 2.7	0.20	20 " 25
87	0.02	"	"	1.25	2.8 " 3.75	0.25	20 " 25
88	0.02	"	"	1.25	4.15 " 4.75	1.00	[illegible]
89	0.02	"	"	1.25	3.4 " 5.5	2.00	20 " 25
90	0.01	"	"	1.25	5.2 " 8.0	0.07	20 " 25
91	0.01	"	"	1.25	4.4 " 5.0	0.30	20 " 25
92	0.01	"	"	1.25	5.0 " 5.5	1.00	20 " 25
93	0.005	"	"	1.25	7.0 " 7.5	0.25	20 " 25
94	0.005	"	"	1.25	8.5 " 9.0	0.50	20 " 25
95	0.005	"	"	1.25	8.0 " 9.0	1.00	20 " 25
96	0.004	"	"	1.25	8.1 " 8.4	0.25	20 " 25
97	0.003	"	"	1.25	8.5 " 9.0	0.50	20 " 25
98	0.001	"	"	1.25	8.5 " 8.7	0.25	20 " 25
99	0.001	"	"	1.25	10.4 " 10.6	0.50	20 " 25
100	0.02	"	"	1.5	2.5 " 3.8	0.25	20 " 25
101	0.02	"	"	1.5	4.0	0.50	20 " 25
102	0.02	"	"	1.5	5.0 " 7.0	1.00	20 " 25

Electrolyte V: { 20 c.c. conc. lactic acid; 16.18 gm. vanadic acid; Make up to 500 c.c. with water. } Dissolve.

TABLE X.

No.	Concentration V_2O_5 gm. c.c.	Electrodes		Area of Cathode in sq. in.	Volts	Amperes	Temperature		Current Density per sq. in.	Time	RESULTS	REMARKS
		Cathode	Anode				° C.	° F.				
67	0.032	Platinum	Platinum	1.25	23 to 11	0.25	19 to 66	66.2 to 150.8	0.2	0 hr. 55 min.	No deposit. Electrolyte stayed blue.	
68	0.032	"	"	1.25	21 " 25	0.50	66 " 74	150.8 " 165.2	0.4	1 " 10 "	Black film on cathode. Electrolyte stayed blue. No V. in deposit.	
69	0.032	"	"	1.25	28.5 " 26.5	0.75	65 " 75	149 " 167	0.6	1 " 0 "	Same.	
70	0.032	"	"	1.25	32 " 22	1.00	75 " 82	167 " 179.6	0.8	1 " 0 "	"	
71	0.032	"	"	1.25	49 " 57	2.00	82 " 109	179.6 " 215.6	1.6	0 " 30 "	"	
72	0.016	"	"	1.25	62 " 39.5	0.25	18 " 52	64.4 " 125.6	0.2	0 " 15 "	"	
73	0.016	"	"	1.25	64.5 " 49	0.50	52 " 78	125.6 " 172.4	0.4	0 " 15 "	"	
74	0.016	"	"	1.25	78.5 " 79.5	1.00	78 " 88	172.4 " 190.4	0.8	0 " 15 "	"	
75	0.008	"	"	1.25	52 " 38	0.25	51 " 73	123.8 " 163.4	0.2	0 " 20 "	"	
76	0.008	"	"	1.25	68 " 60	0.50	73 " 80	163.4 " 176	0.4	0 " 15 "	"	
77	0.008	"	"	1.25	110 "114	1.00	80 " 91	176 " 195.8	0.8	0 " 15 "	"	
79	0.004	"	"	1.25	64 " 56	0.25	54 " 75	129.2 " 167	0.2	0 " 15 "	"	
80	0.004	"	"	1.25	91 " 92	0.50	75 " 90	167 " 194	0.4	0 " 15 "	"	
81	0.002	"	"	1.25	94 " 72	0.25	54 " 73	129.2 " 163.4	0.2	0 " 35 "	"	
82	0.002	"	"	1.25	110	0.40	73 " 88	163.4 " 190.4	0.32	0 " 20 "	"	
83	Lactic acid (conc.) saturated with vanadic acid, did not permit the current to pass under any conditions.											
84	0.032	Platinum	Pt. Wire	1.5	44 to 24	0.25	33 to 52	91.4 to 125.6	0.17	1 " 13 "	Dark brown deposit on cathode showing vanadium	The amount of deposit formed was small. On igniting gave organic odor and formed little globules on the cathode.
85	0.032	"	"	1.5	41	0.50	52 " 63	125.6 " 145.4	0.34	1 " 0 "	Same.	Used fish skin as partition.
86	0.032	"	"	1.5	65 " 60	1.00	63 " 68	145.4 " 154.4	0.68	1 " 40 "	"	Cathode liquor, lactate solution. Anode liquor-water + 20 c.c. lactate solution.

TABLE XI.

Electrolyte VI: 20 c.c. of Ethyl-sulphuric acid is saturated with 10 gm. vanadic acid. Made up to 500 c.c. with water.

87	0.02	Platinum	Platinum	1.25	2.6 to 2.5	0.25	19 to 65	66.2 to 149	0.2	0 hr. 55 min.	No deposition. Electrolyte from light green to blue.	
88	0.02	"	"	1.25	2.9 " 3.5	0.50	57 " 65	134.6 " 149	0.4	1 " 10 "	Same.	
89	0.02	"	"	1.25	3.8 " 3.75	0.75	49 " 60	120.2 " 140	0.6	1 " 0 "	"	
90	0.02	"	"	1.25	4.15 " 4.00	1.00	61	141.8	0.8	1 " 0 "	"	
91	0.02	"	"	1.25	5.4 " 5.3	2.00	58 " 61	136.4 " 141.8	1.6	0 " 30 "	"	
92	0.01	"	"	1.25	3.4 " 4.6	0.25	18 " 31	64.4 " 87.8	0.2	0 " 15 "	"	
93	0.01	"	"	1.25	4.4 " 3.9	0.50	31 " 58	87.8 " 136.4	0.4	0 " 15 "	"	
94	0.01	"	"	1.25	5.9 " 5.4	1.00	58 " 82	136.4 " 179.6	0.8	0 " 15 "	"	
95	0.005	"	"	1.25	3.9 " 3.6	0.25	54 " 69	129.2 " 156.2	0.2	0 " 20 "	"	
96	0.005	"	"	1.25	5.2 " 6.1	0.50	69 " 85	156.2 " 185	0.4	0 " 15 "	"	
97	0.005	"	"	1.25	7.6 " 6.6	1.00	83	181.4	0.8	0 " 15 "	"	
98	0.003	"	"	1.25	6.3 " 6.4	0.25	52 " 65	125.6 " 149	0.2	0 " 15 "	"	
99	0.003	"	"	1.25	8.2 " 9.2	0.50	65 " 73	149 " 163.4	0.4	0 " 15 "	"	
100	0.001	"	"	1.25	8.9 " 8.7	0.25	50 " 72	122 " 161.6	0.2	0 " 35 "	"	
101	0.001	"	"	1.25	12.4 " 13.4	0.40	72 " 82	161.6 " 179.6	0.32	0 " 20 "	"	
102	0.02	"	"	1.5	4.4 " 3.8	0.25	36 " 56	96.8 " 132.8	0.17	1 " 13 "	No deposit. Electrolyte green to blue.	Used fish skin as partition. Cathode liquor—vanadian liquor.
103	0.02	"	"	1.5	5.0	0.50	56 " 62	132.8 " 143.6	0.34	1 " 0 "	Same.	Anode—water + 10 c.c. vanadium liquor.
104	0.02	"	"	1.5	8.0 " 7.6	1.00	62 " 66	143.6 " 150.8	0.68	1 " 40 "	"	

Electrolyte V: 20 c.c. conc. lactic acid, 10.13 gm. vanadic acid, Make up to 500 c.c. with water. Dissolve.

No.	Concentration V₂O₅ gm. c.c.	Electrodes: Cathode	Electrodes: Anode	Area of Cathode in sq. in.	Time	Amperes	Temperature °C.
67	0.032	Platinum	Platinum	1.27	21 to 11	0.25	19 to [illegible]
68	0.032	"	"	1.25	" 45	0.50	[illegible] " [illegible]
69	0.032	"	"	1.25	[illegible] " 2½	0.75	[illegible] " [illegible] 140
70	0.032	"	"	1.25	36 " 45	1.00	[illegible] " [illegible] 102
71	0.032	"	"	1.25	48 " 37	2.00	22 " 102 [illegible]
72	0.016	"	"	1.25	[illegible] " 3½	0.25	[illegible] " 54 [illegible]
73	0.016	"	"	1.25	64 " 40	0.50	52 " 73 [illegible]
74	0.016	"	"	1.25	78.5 " 73.5	[illegible]	58 " 83 [illegible]
75	0.008	"	"	1.25	52 " 48	0.25	[illegible] " 73 [illegible]
76	0.008	"	"	1.25	68 " 60	0.50	73 " 90 [illegible]
77	0.008	"	"	1.25	110 " 105	1.00	80 " 91 [illegible]
78	0.004	"	"	1.25	84 " 56	0.25	[illegible] " 73 [illegible]
79	0.004	"	"	1.25	91 " 92	0.50	75 " 90 [illegible]
80	0.002	"	"	1.25	98 " 72	[illegible]	[illegible] " 93 [illegible]
81	0.002	"	"	1.25	110	0.40	[illegible] " 81 [illegible]
82	Lactic acid (conc.) saturated with vanadic acid, did not permit the electrolyte to pass [illegible]						
83	0.022	Platinum	Pt. Wire	1.5	44 to 24	0.25	[illegible] to 20 [illegible]
84	0.022	"	"	1.5	41	0.50	[illegible] " 63 [illegible]
85	0.022	"	"	1.5	65 " 41	1.00	[illegible] " 68 [illegible]

Electrolyte VI: 20 c.c. of lithyl-sulphuric acid is saturated with 10 gm. vanadic acid. Dissolve.

No.	Concentration V₂O₅ gm. c.c.	Electrodes: Cathode	Electrodes: Anode	Area of Cathode in sq. in.	Time	Amperes	Temperature °C.
86	0.02	Platinum	Platinum	1.25	2.0 to 2.5	0.25	[illegible] to [illegible]
87	0.02	"	"	1.25	2.0 " 1.5	0.50	[illegible] " [illegible]
88	0.02	"	"	1.25	2.8 " 2.05	0.75	30 " 60 [illegible]
89	0.02	"	"	1.25	4.15 " 4.00	1.00	[illegible] [illegible]
90	0.02	"	"	1.25	5.4 " 5.3	2.00	38 " 61 [illegible]
91	0.01	"	"	1.25	5.4 " 4.6	0.25	15 " 27 [illegible]
92	0.01	"	"	1.25	7.4 " 2.9	0.50	[illegible] " [illegible] [illegible]
93	0.01	"	"	1.25	5.9 " 5.4	1.00	38 " 47 [illegible]
94	0.005	"	"	1.25	5.9 " 7.0	0.25	[illegible] " 9 [illegible]
95	0.005	"	"	1.25	8.2 " 8.1	0.50	40 " 35 [illegible]
96	0.005	"	"	1.25	8.0 " 8.5	1.00	[illegible] [illegible]
97	0.003	"	"	1.25	8.4 " 9.1	0.25	[illegible] " [illegible] [illegible]
98	0.003	"	"	1.25	9.1 " 9.2	0.50	[illegible] " 74 [illegible]
99	0.003	"	"	1.25	8.9 " 8.7	0.75	30 " [illegible] [illegible]
100	0.001	"	"	1.25	12.4 " 13.4	0.40	72 " [illegible] [illegible]
101	0.001	"	"	1.25	14.4 " 3.8	0.25	30 " [illegible] [illegible]
102	0.02	"	"	1.5	5.0	0.50	[illegible] " [illegible] [illegible]
103	0.02	"	"	1.5	5.0 " 7.5	1.00	[illegible] " [illegible] [illegible]
104	0.02	"	"	1.5	[illegible]	[illegible]	[illegible]

Electrolyte VII: Dissolve 10 gm. of tartaric acid in 80 c.c. water. Use 70 c.c. Then add vanadic acid in portions of 1 gm. during electrolysis.

TABLE XII.

No.	Concentration V_2O_5 gm. c.c.	Electrodes		Area of Cathode in sq. in.	Volts	Amperes	Temperature		Current Density per sq. in.	Time	RESULTS	REMARKS
		Cathode	Anode				° C.	° F.				
105	0.014	Platinum	Platinum	0.9	13.4 to 9.0	0.25	20 to 49	68 to 120.2	0.28	0 hr. 15 min.	No deposit. Electrolyte sapphire blue.	Electrolyte blue at start, and never changed in color in any of the experiments from 105 to 123.
106	0.014	"	"	0.9	13.5 " 12.1	0.50	49 " 67	120.2 " 152.6	0.56	0 " 15 "	Same.	
107	0.014	"	"	0.9	22 " 23	1.00	67 " 81	152.6 " 177.8	1.12	0 " 15 "	"	
108	0.028	"	"	0.9	5.8 " 6.6	0.25	69	156.2	0.28	0 " 15 "	"	
109	0.028	"	"	0.9	10.2 " 10.8	0.50	69 " 75	156.2 " 167	0.56	0 " 15 "	"	
110	0.028	"	"	0.9	18.5 " 19.3	1.00	75 " 98	167 " 208.4	1.12	0 " 15 "	"	
111	0.028	"	"	0.9	25.0 " 26.0	2.00	98	208.4	2.24	0 " 10 "	"	
112	0.056	"	"	0.9	4.5 " 4.8	0.25	80	176	0.28	0 " 15 "	"	
113	0.056	"	"	0.9	7.7 " 7.8	0.50	80 " 87	176 " 188.6	0.56	0 " 15 "	"	
114	0.056	"	"	0.9	15.5	1.00	87	188.6	1.12	0 " 15 "	"	
115	0.112	"	"	0.9	4.5 " 5.7	0.25	81 " 67	177.8 " 152.6	0.28	0 " 13 "	"	
116	0.112	"	"	0.9	9.9 " 10	0.50	67 " 77	152.6 " 170.6	0.56	0 " 15 "	"	
117	0.112	"	"	0.9	17.5 " 15	1.00	77 " 79	170.6 " 174.2	1.12	0 " 15 "	"	
118	0.224	"	"	0.9	4.5	0.25	79 " 69	174.2 " 156.2	0.28	0 " 10 "	"	
119	0.224	"	"	0.9	9.8 " 10	0.50	69 " 73	156.2 " 163.4	0.56	0 " 15 "	"	
120	0.224	"	"	0.9	18 " 16.5	1.00	73 " 80	163.4 " 176	1.12	0 " 15 "	"	
121	0.448	"	"	0.9	5.4 " 6.2	0.25	80 " 73	176 " 163.4	0.28	0 " 15 "	"	
122	0.448	"	"	0.9	10.6 " 10.2	0.50	73 " 77	163.4 " 170.6	0.56	0 " 15 "	"	
123	0.448	"	"	0.9	21.5 " 19	1.00	77 " 81	170.6 " 177.8	1.12	0 " 15 "	"	

Electrolyte: Dissolve 5 gm. vanadic acid in 5 gm. dehydrated sodium carbonate. Make up to 250 c.c. with water and add 1 gm. sodium sulphide.

TABLE XIII.

No.	Concentration V_2O_5 gm. c.c.	Electrodes		Area of Anode in sq. in.	Volts	Amperes	Temperature		Current Density per sq. in.	Time	RESULTS	REMARKS
		Cathode	Anode				° C.	° F.				
1	0.02	Platinum	Carbon	3.75	10 to 9.9	1.0	29 to 56	84.2 to 132.8	0.27	0 hr. 35 min.	No deposit on cathode. Catholyte yellowish at start; orange-brown at end.	Used porous cup. Cathode liquor: the vanadium solution. Anode liquor: water + sodium carbonate.
2	0.02	"	"	3.75	14 " 13.3	2.0	72 " 73	161.6 " 163.4	0.54	2 " 0 "	Same.	Same conditions.
3	0.004	"	"	3.75	10.3 " 9.6	1.0	33 " 57	91.4 " 134.6	0.27	0 " 35 "	"	Same conditions.
4	0.004	"	"	3.75	15 " 14.5	2.0	66	150.8	0.54	2 " 0 "	"	

Electrolyte 1[illegible]: Dissolve 10 gm. of tartaric acid in 80 c.c. water. Use 20 c.c. Tartaric acid remains acid in portions of 1 c.c. during electrolysis.

No.	Concentration V.O. per c.c.	Electrodes Cathode	Electrodes Anode	Area of Cathode in sq. in.	Volts	Amperes	Temperature °C.
105	0.014	Platinum	Platinum	1.0	1.4 to 9.0	0.25	20 to 7[illegible]
106	0.014	"	"	0.9	1.5 " 12.1	0.50	19 " 6[illegible]
107	0.014	"	"	0.9	22 " 23	1.00	6[illegible] " 81
108	0.025	"	"	0.9	23 " 6.5	0.25	69
109	0.025	"	"	0.9	10.2 " 10.8	0.50	69 " 75
110	0.025	"	"	0.9	18.5 " 19.4	1.00	75 " 98
111	0.025	"	"	0.9	25.0 " 26.0	2.00	95
112	0.050	"	"	0.9	1.5 " 4.8	0.25	95
113	0.050	"	"	0.9	7.5 " 7.8	0.50	95 " 97
114	0.050	"	"	0.9	12.5	1.00	95
115	0.125	"	"	0.9	5.5 " 5.7	0.25	85 " 87
116	0.125	"	"	0.9	8.5 " 10	0.50	85 " 87
117	0.125	"	"	0.9	12.5 " 15	1.00	75 " 76
118	0.250	"	"	0.9	4.5	0.25	70 " 75
119	0.250	"	"	0.9	9.2 " 10	0.50	69 " 73
120	0.250	"	"	0.9	18 " 19.5	1.00	75 " 80
121	0.440	"	"	0.9	5.4 " 6.2	0.25	80 " 72
122	0.440	"	"	0.9	10.5 " 10.2	0.50	75 " 77
123	0.440	"	"	0.9	21.5 " 19	1.00	77 " 81

Electrolyte: Dissolve 5 gm. vanadic acid in 5 gm. dehydrated sodium carbonate. Make up to 200 c.c. with water and add 1 gm. sodium sulphate.

No.	Concentration V.O. per c.c.	Electrodes Cathode	Electrodes Anode	Area of Anode in sq. in.	Volts	Amperes	Temperature °C.
1	0.05	Platinum	Carbon	1.25	10 to 9.0	1.0	20 to 5[illegible]
2	0.05	"	"	3.25	14 " 12.2	2.0	72 " 73
3	0.05	"	"	3.25	10.3 " 9.5	1.0	71 " 57
4	0.05	"	"	3.25	15 " 14.5	2.0	95

strongly contaminated by small yellow crystals, probably a complex potassium vanadate, that it was impossible to figure the anode efficiency. The small crystals at the anode were not an anode product, but separated from the anolyte, collecting to a great extent at the bottom of the porous cup. This is simply a case of super-saturation of the anolyte in respect to the crystalline compound. In experiment No. 66 an endeavor was made to prepare an anolyte, using ammonia as the solvent for vanadic oxide. This was found to be impossible, as even with an addition of 30 c.c. of hydrogen peroxide the practically insoluble ammonium metavanadate crystallized from the solution.

A series of tests were then run to investigate the effect of other oxides on the deposit. In each case 20 grams of vanadic oxide were mixed with 10 grams of the oxide in question. Mixtures of vanadic oxide with ferric oxide (Fe_2O_3), cuprous oxide (Cu_2O), mixtures of the two, manganese dioxide (MnO_2), lead peroxide (PbO_2), silica (SiO_2), lime (CaO), magnesia (MgO), alumina (Al_2O_3), zinc oxide (ZnO), arseneous oxide (As_2O_3) and with uranic oxide (UO_3). These mixtures of oxides were treated with 8.97 grams sodium hydroxide in 100 c.c. of water, containing 10 c.c. of hydrogen peroxide (3 percent by volume) similarly as when vanadic oxide was used alone. The solutions thus obtained were then used as anolytes in porous cups. The catholyte in each case was a dilute sodium hydroxide solution. The anodes were platinum foil and the cathodes carbon rods. The anode current densities were 30 amperes per sq. ft. (3.3 amp. per sq. dm.) and the temperature varied from 80° to 94° C. The anolyte in each case was the filtrate obtained by leaching the mixed oxides with the alkaline solution. These solutions were tested for the presence of the admixed element. The residue left on the filter paper was tested for vanadium.

When a mixture of ferric oxide and vanadic oxide were treated as above described, the filtrate obtained showed no trace of iron. The residue, after careful washing, showed only a trace of vanadium. The deposit obtained by electrolysis was brick red in color, adhered to the anode and was free from iron. The anode ampere efficiency was 96.17 percent.

Cuprous oxide is partly dissolved in the alkaline leaching solution forming in all probability the hydroxide which is soluble

in the alkaline solution. It is highly improbable that copper metavanadate is in the solution, as this compound is only slightly soluble in alkaline solutions. The copper in the solution did not interfere with the anode deposit, no trace being found in the carefully washed anode product. The residue left after leaching and careful washing showed the presence of a small amount of undissolved vanadic oxide, indicating that the leaching was not quite complete. This in all probability is due to the fact that some of the alkali was used to form the hydrated oxide of copper. The deposit was normal and the anode ampere efficiency was 95.68 percent.

The anolyte obtained by leaching a mixture of the oxide of vanadium, iron (ic) and copper (ous) contained some copper, but no iron. The anode product of hydrated vanadic oxide contained neither iron nor copper after thorough washing. The residue from leaching the mixed oxides was washed, dried and tested for vanadium. Only a trace of vanadium could be detected. The anode deposit was normal, the anode ampere efficiency being 96.03 percent.

Manganese dioxide is attacked by the alkali leaching solution, forming either the manganese metavanadate with the vanadic oxide present or the hydroxide $Mn(OH)_2$ or both. These compounds are practically insoluble in alkalies. Only a trace of manganese could be detected in the anolyte. The residue left after leaching indicated that quite an amount of vanadic oxide had not been dissolved. The anode product showed no manganese, but it was darker in color than other anode products and somewhat slimy in appearance. This appearance of the anode product is undoubtedly due to the small amount of the manganese in solution. The amount of manganese in the deposit was, however, so small that it was impossible to detect it. The anode ampere efficiency was 80.79 percent. Evidently the presence of a small amount of manganese in the anolyte reduced the anode current efficiency.

Lead peroxide seemed to have some effect on the leaching. This compound forms alkali plumbates, soluble in alkalies, and also a vanadate. Some lead vanadate had evidently formed, as the leaching was incomplete. The anolyte after leaching indicated no abnormality, no lead being found in the filtrate, but some vana-

dium remained in the residue. The anode deposit was normal. The anode ampere efficiency was 79.13 percent.

Silica interferes materially with the leaching. Some silica enters the anolyte, but this does not affect the anode deposit. The residue after leaching has a yellowish-white appearance after washing and drying. On dissolving in acid the residue gives a red solution which shows vanadium strongly. The anode ampere efficiency was 69.96 percent. The anode deposit was normal.

Lime (CaO) resembles silica in its behavior. The anolyte showed the presence of calcium. The residue left from leaching has a yellowish-white appearance and dissolves in dilute acids with a red color, and gives a strong test for vanadium. This indicates that the residue is calcium vanadate. The anode ampere efficiency was 7.63 percent. This very low anode current efficiency proves that only very little vanadic oxide had been dissolved by the leaching solution. The anode product was brick red in color and adhered to the anode. After careful washing no calcium could be detected in the deposit.

Magnesia (MgO) forms a magnesium vanadate which is slightly soluble in the alkaline solution, and re-precipitates on heating. The residue left after leaching was yellowish-white in appearance and dissolved in dilute acids, forming a red-colored solution giving a strong vanadium reaction. The anode ampere efficiency was low, 26.82 percent. The deposit had a brick red color and adhered to the anode.

Alumina (Al_2O_3) behaved similarly to lime and magnesia, some entering the anolyte, while most of it stayed on the filter paper as a yellowish-white residue which dissolved in dilute acids, forming a red colored solution, and showed vanadium strongly. The anode ampere efficiency was 24.99 percent. The deposit was dark red, giving partly a colloidal solution and partly adherent deposit.

The oxide of zinc interferes only slightly with the leaching. Not all of the vanadic oxide was dissolved, but the vanadium reaction for the residue was much less than for silica, lime, magnesia or alumina. No zinc was detected in the anolyte. The anode ampere efficiency was 95.85 percent, the deposit being brick red and adhering well to the anode.

Arsenious oxide (As_2O_3) forms a greenish vanadate with

vanadic oxide, which is slightly soluble in the leaching solution. The anode deposit obtained was gelatinous and adhered in part to the anode in a thin film, while some stayed in the anolyte in form of a colloid. The anode ampere efficiency was very low, and the deposit contained a large percentage of arsenic.

Uranic oxide (UO_3) prevented the complete extraction of vanadic oxide, some vanadic oxide remaining undissolved in the residue. No uranium could be detected in the anolyte, which had an oily appearance. The anode current efficiency was 96.20 percent, the deposit being brick red in color and adhering firmly to the anode.

Conclusions. The preliminary 33 experiments indicate that an oxidation takes place at the anode, the anode product which tends to form being of an orange red to brick red color. Platinum hydride is formed on a platinum cathode, which increases in amount as the current density increases, and as the time of the run is increased. The electrolyte changes from a faint yellow to an orange yellow, the color being due to the product formed at the anode redissolving. With increased concentration of vanadic oxide in the electrolyte, a red deposit formed on the anode, dissolving until the electrolyte was dark orange yellow, and then remaining as such on the anode. This suggested that if the anolytes and the catholytes were kept separate by porous partitions the yield of the anode product might be increased. This was done in experiments Nos. 34 to 66.

In experiments Nos. 34 to 40 it was apparent that the yield of the anode product of hydrated vanadic oxide materially increased as the orange coloration of the electrolyte increased. As the change from the practically colorless sodium metavanadate anolyte to that of the orange state was due to oxidation at the anode, hydrogen peroxide (3 percent by volume) was added to the sodium hydroxide solution in small quantities (5 to 10 c.c. per 100 c.c. of anolyte). The addition of the hydrogen peroxide accomplished the desired oxidizing effect, thus saving at least two hours and 18 minutes in obtaining the anode deposit, according to experiment No. 34, during which time no deposition took place in this test. The effect of an addition of hydrogen peroxide under the same current density conditions as in No. 34 is shown in experiment No. 46.

That a reaction is taking place in the anolyte in the course of electrolysis, affecting the deposition at the anode, may be observed from the volt time-curves Nos. I, II and III, for data see Table XIV. Three specific cases are considered. Curve I shows the effect of hydrogen peroxide on the anode deposition of hydrated vanadic oxide. The data is taken from experiment No. 48, using an anolyte containing per c.c. 0.2 gram of vanadic oxide, 0.09 gram sodium hydroxide and 0.05 c.c. of hydrogen peroxide (3 percent by volume). Deposition on the anode started practically as soon as the current passed, the color of the anolyte at the start being orange yellow. The voltage drop from A to B is due to the temperature rising to 92° C. From B to C normal anode deposition took place, the product adhering to the anode. From C to D the anode product changed to the colloidal state.

Curve II represents the action taking place in an anolyte containing per c.c. 0.2 gram of vanadic acid, 0.23 gram of sodium hydroxide and no hydrogen peroxide. The current density was kept constant at 30 amperes per sq. ft. (3.3 amp. per sq. dm.). From A to B a drop in voltage took place, due to the rise in temperature. From B to C no deposition occurred, the anolyte absorbing oxygen. At C the anolyte was in its higher state of oxidation, the color of the solution changing from light yellow to orange during the period C to D, due to the anolyte becoming saturated with the hydrated vanadic oxide. The deposition on the anode proceeded normally between D and E.

Curve III, experiment 37, illustrates the anode reactions which occur in an identical anolyte to that used in experiment No. 47, but at lower anode current density. The anode current density was kept constant at 15 amperes per sq. ft. (1.7 amp. per sq. dm.). During period A to B a slight rise in potential resulted, due to a slight drop in temperature (94° to 85° C.). During period B to C no deposition took place, but oxidation of the anolyte occurred similar to that during period B to C in experiment No. 47, Curve II. The period C to D, during which the anolyte was being saturated with the hydrated vanadic oxide, shows the saturation taking place when the anolyte changed from colorless to orange color, which is completed at D. Anode deposition took place between period D and E.

Table XIV.

Curve I.

Exp. No. 48. Dissolved 20.02 grams of vanadic oxide in 100 c.c. of water containing 8.97 grams of sodium hydroxide and 5 c.c. hydrogen peroxide (3 percent by volume), used as anolyte. Anode current density 0.21 amperes per sq. in. (30 amperes per sq. ft or 3.3 amperes per sq. dm.).

Curve II.

Exp. No. 47. 20.02 grams vanadic oxide dissolved in 100 c.c. of water containing 22.72 grams of sodium hydroxide, used as anolyte. Anode current density 0.21 amperes per sq. in. (30 amperes per sq. ft. or 3.3 amperes per sq. dm.).

Curve III.

Exp. No. 37. 20.02 grams vanadic oxide dissolved in 100 c.c. of water containing 22.72 grams hydroxide, used as anolyte. Anode current density 0.107 ampere per sq. in. (15 amperes per sq. ft. or 1.7 ampere per sq. dm.).

Curve I		Curve II		Curve III	
Time in Minutes	Volts	Time in Minutes	Volts	Time in Minutes	Volts
0	4.9	0	4.0	0	2.65
8	4.6	8	3.8	7	2.85
9	4.45	60	3.4	15	2.85
51	4.4	15	3.4	20	2.85
15	4.3	37	3.4	30	2.85
37	4.4	23	3.4	30	2.85
23	4.3	30	3.4	30	2.85
30	4.3	30	3.65	30	3.05
30	4.4	15	3.92	30	3.18
30	4.55	15	4.05	30	3.2
30	5.7	5	4.1	12	3.55
		5	4.05	28	3.35
		5	4.05	30	3.35
		5	4.05	30	3.3
		5	4.1	30	3.4
		5	4.1	30	3.35
				30	3.35
				30	3.30

Curves II and III show clearly that a reaction takes place in the anolyte, and that the speed of this reaction may be increased by increasing the anode current density. By comparing the anode ampere efficiencies of experiments Nos. 37, 47 and 48, it is observed that in 48 the anode ampere efficiency was the highest, this being due to the yellow state of the anolyte at the start. This is also indicated by Curve I, deposition taking place at the anode

from the very start of electrolysis, proving that the higher state of oxidation of the anolyte is essential for high anode current efficiency. These experiments and curves also show that the most suitable chemical oxidizing agent is hydrogen peroxide.

Another benefit is derived by the use of hydrogen peroxide as an oxidizing agent. Whereas, in experiment No. 34, it took 0.23 gram of sodium hydroxide per c.c. of water to dissolve 0.2 gram of vanadic oxide, it took only 0.09 gram of sodium hydroxide in experiment No. 46 to accomplish the same result. This means a saving of 153.3 percent of sodium hydroxide.

Experiments Nos. 41 to 46 show the effect of current density on the yield and on the anode ampere efficiency. The yield at the anode decreases as the current density decreases, while the anode ampere efficiency is only slightly influenced. The yield varies from 1.4903 grams vanadic oxide for anode current density of 7 amperes per sq. ft. (0.8 amp. per sq. dm.) to 6.2217 grams for anode current density of 30 amperes per sq. ft. (3.3 amp. per sq. dm.), the anode ampere efficiencies varying only between 92.78 percent and 96.29 percent, the higher anode current density giving the higher efficiency.

By comparing the results of electrolysis of a neutral, a slightly alkaline and a strongly alkaline anolyte (see experiments Nos. 47 and 48, also 49, it was found that the neutral anolyte gives the best yield and the highest anode ampere efficiency. A high anode ampere efficiency and a high yield of electrolytic vanadic oxide can only be obtained by using a non-alkaline oxidizing agent such as hydrogen peroxide, with the theoretical amount of sodium hydroxide (NaOH), in a practically neutral anolyte.

Hydrogen peroxide was found to be the most satisfactory chemical oxidizer for the preparation of the sodium metavanadate anolyte, as by its use a neutral anolyte may be obtained. Electrolytes thus prepared yielded high anode ampere efficiency.

Sodium peroxide was found to be less satisfactory than hydrogen peroxide as an oxidizer, as by its use a slightly alkaline anolyte resulted. The slight alkalinity reduced the anode ampere efficiency, and had a tendency to cause the anode deposit to become colloidal.

Potassium chlorate and chloride of lime, when used as chemical oxidizers for the preparation of the sodium metavanadate solu-

tion, gives an anolyte from which chlorine is liberated, which has a markedly deleterious effect on the anode deposits. Potassium permanganate was found to be an unsatisfactory oxidizer, as by its use the anode ampere efficiency was lowered, and the anode deposit of hydrated vanadic oxide was rendered impure.

The effect of concentration of the metavanadate anolyte was studied in experiments Nos. 54 to 57. The concentrations used were 0.075 to 0.2 gram vanadic acid per c.c. It was observed that, with a decrease in concentration, the yield of the anode deposit decreased. As lead anodes were employed, the anode ampere efficiency could not be obtained, because the anode product was contaminated with lead, and it was impossible to obtain a relatively pure vanadic oxide.

On comparing the effect of high anode current densities, 60 amperes per sq. ft. (6.6 amp. per sq. dm.), with anolytes containing 0.2 gram of vanadic acid per c.c., it was observed that the anode yield increased with increase in current density, whether hydrogen peroxide or sodium peroxide were used as an oxidizing agent. The increase in the anode yield by doubling the current was, however, not double that of the experiments in which 30 amperes per sq. ft. (3.3 amp. per sq. dm.) was used. Comparing experiments Nos. 42 and 58, it is observed that the yield in test 48 would be 5.3285 grams of vanadic oxide at the end of two hours and 40 minutes. In test 58 the yield for the same length of time was 9.6709 grams. That the yield in No. 58 was not double the one of 42 was due to the lower ampere efficiency of the first, which was only 84.22 percent, while that of the latter was 92.78 percent. By the use of sodium peroxide as an oxidizing agent the yield and the anode ampere efficiency were still less (see experiment No. 59), being 8.457 grams vanadic oxide; efficiency, 80.29 percent. In this last test the yield and anode ampere efficiency, besides being affected by the high current density, is furthermore influenced by the slight alkalinity of the anolyte, due to the sodium peroxide (Na_2O_2). In both experiments, Nos. 58 and 59, it was clearly shown that very high temperature (above 92° C.) and high anode current densities tend to make the anode deposit colloidal, especially so if the anolyte is slightly alkaline.

In experiments Nos. 60 to 62 it was found that chemically pure

sodium metavanadate anolyte only gave a high ampere efficiency and a high yield of hydrated vanadic oxide after the anolyte had attained the orange yellow state—differing in this respect from experiments Nos. 34 to 40, in so far that the length of time required to obtain the orange yellow state was less. This higher anode efficiency of experiments Nos. 60 to 62 was due to the chemically pure sodium metavanadate solution being neutral, while in tests Nos. 34 to 40 the anolyte was strongly alkaline.

On comparing the solubility of vanadic oxide in solutions of sodium hydroxide, potassium hydroxide, ammonium hydroxide, to each of which hydrogen peroxide was added as the oxidizing agent, and sodium peroxide alone, it was found that the solution of sodium hydroxide plus hydrogen peroxide gave the most satisfactory results in every respect, giving the highest anode ampere efficiency and the best yield of electrolytic vanadic oxide. It was of value to compare the amounts of the alkalies required to dissolve the same amount of vanadic oxide, a solution of 8.97 grams of sodium hydroxide (98 percent pure) in 100 c.c. of water containing 5 c.c. of hydrogen peroxide completely dissolved 20 grams of vanadic oxide. In order to dissolve the same quantity of vanadic oxide it required 6.9 grams of 100 percent sodium peroxide in 100 c.c. of water; also a solution of 12.31 grams of potassium hydroxide in 100 c.c. of water containing 16 c.c. of hydrogen peroxide dissolved 20 grams of vanadic oxide. While it requires less sodium peroxide than of sodium hydroxide plus hydrogen peroxide, the great disadvantage of the first solvent is that its price is prohibitive, and the anode current efficiency is slightly lower, being 93.58 percent for the sodium peroxide solution, as compared with 96.63 percent for the sodium hydroxide plus hydrogen peroxide solution. Potassium hydroxide not only dissolves less vanadic oxide per sodium hydroxide equivalent, but it is also more expensive, and furthermore, it requires a larger amount of hydrogen peroxide. The product of electrolytic vanadic oxide from potassium hydroxide anolyte is contaminated with an insoluble potassium vanadate compound, which separates from the anolyte during the electrolysis. Ammonium hydroxide could not be used as solvent for vanadic oxide because, as soon as some vanadic oxide dissolved, it formed the insoluble ammonium meta-

vanadate, which precipitated out and collected at the bottom of the receptacle.

Regarding the commoner associates of vanadium in ores, it may be said that the oxides of the alkaline earth metals (such as calcium and magnesium) interfere materially with the extraction of the vanadic oxide with solutions of sodium hydroxide containing hydrogen peroxide; they cause very poor extraction, and low anode ampere efficiencies. Iron oxide seems to have no ill effect, if present as ferric oxide (Fe_2O_3), but if present as a soluble salt the alkaline leaching solution precipitates the iron as hydroxide ($Fe(OH)_3$), and more leaching solution would be required to extract the vanadic oxide. A small amount of manganese in the anolyte causes the anode product to have a dark color, decreases the ampere efficiency and lowers the yield of electrolytic vanadic oxide.

Copper as oxide has very little effect on the extraction of vanadium by solutions of sodium hydroxide plus hydrogen peroxide. The extraction of the vanadic oxide is rapid, and it is due to this that copper does not enter the anolyte as soluble copper hydroxide. Lead peroxide interferes with the extraction, lowering the solubility of the vanadic oxide, but only a trace, if any, lead peroxide dissolved. The solution, on electrolysis, gave a pure anode product, but a low anode ampere efficiency. Alumina and silica behave similarly to the alkaline earth metal oxides, reducing the extraction and lowering the anode ampere efficiency. The anode product was slimy and very hard to handle. Zinc oxide slightly decreased the extraction, and only slightly affected the anode ampere efficiency. No zinc could be detected in the anolyte, and the anode deposit was normal in every respect. Arsenious oxide (As_2O_3) forms a complex compound with vanadic oxide, which is slightly soluble in the alkaline leaching solution. It caused a low anode ampere efficiency and a gelatinous anode deposit. Uranic oxide decreased the extraction of vanadic oxide to some extent, and gave an oily solution free from uranium. The anode ampere efficiency was high.

The low ampere efficiency is generally due to bad leaching giving an anolyte of too low a concentration in vanadic oxide. In every respect it is better to treat materials low in alkaline earths, silica and alumina. The presence of manganese oxide in very

small amounts is deleterious. Iron, copper and zinc have little ill effect if present as oxides, the leaching being so rapid that none, or only a small amount, of these are dissolved by the alkaline leaching agent. Arsenic should be absent. In general it is better to treat a concentrated product containing vanadic oxide with only small amounts of impurities.

The only satisfactory anode is one of platinum. Lead contaminates the anode deposit, while on a carbon anode the product does not adhere. The cathode may be of iron, carbon, lead, copper or platinum. A slight increase in anode yield is obtained by making the cathode area small, so as to increase the oxidizing action at the anode. In all cases an insoluble porous diaphragm must be used in order to separate the anolyte and the catholyte, in order to obtain electrolytic vanadic oxide.

From approximately 60° C. up to 92° C. the anode deposit adheres firmly to the anode, if the anolyte is as nearly neutral as possible. Higher temperatures have a tendency to cause the formation of colloids. Similarly, very high current densities and high temperatures combined have the same effect. A third cause for the formation of colloids is the alkalinity of the anolyte. Finally, the colloidal state of the deposit is promoted by agitation of the anode solution.

In the 368 experiments performed, metallic vanadium was not obtained. The question naturally arises: "What is the cause of this"? Chemically it is known that vanadium oxide is extremely hard to reduce, even in the electric furnace and by the Goldschmidt Thermit process. The latter will, as a rule, reduce the oxides of metals like chromium, manganese and titanium with comparative ease, while the oxides of vanadium are reduced only with the greatest difficulty.

There is very little available information as to the heat of formation of vanadium salts. However, some attempts have been made by Mixter to determine the heat of formation of some of the vanadium oxides. The values obtained by Mixter are only approximations, and should not be considered otherwise. (Mixter: "Heat of Formation of Oxides of Uranium and Vanadium," American Journal of Science, **34**, 141-154). The deductions made to explain the non-deposition of metallic vanadium from aqueous solutions of its salts by means of the electric current are,

therefore, only theoretical. They are simply conclusions drawn from observed facts on other elements.

In the following table are given some heats of formation of oxides, sulphates, chlorides and fluorides.

HEATS OF FORMATION IN GRAM CALORIES.

Element	Oxides		Chlorides		Fluorides		Sulphates	
Silver	Ag_2O:	7000	$AgCl$:	29000	AgF:	22070	Ag_2SO_4:	167100
Copper	CuO:	37700	$CuCl_2$:	51400	CuF_2:	....	$CuSO_4$:	181700
Nickel	NiO:	61500	$NiCl_2$:	74700	NiF_2:	....	$NiSO_4$:	....
Tin	SnO:	70700	$SnCl_2$:	80900	SnF_2	....	....	....
Zinc	ZnO:	84400	$ZnCl_2$:	97400	ZnF_2:	....	$ZnSO_4$:	229600
Manganese ..	MnO:	90900	$MnCl_2$:	112000	MnF_2:	....	$MnSO_4$:	249400
Magnesium...	MgO:	143400	$MgCl_2$:	151200	MgF_2:	209500	$MgSO_4$:	300900
Iron	Fe_2O_3:	195600	$FeCl_3$:	96150	FeF_3:	....	....	....
Aluminium ..	Al_2O_3:	392600	$AlCl_3$:	161800	AlF_3:	....	....	....
Vanadium ...	V_2O_5:	441000	....	....	....	....	....	....
Vanadium ...	V_2O_3:	353200	....	....	....	....	....	....
Vanadium ...	VO:	104300	....	....	....	....	....	....

All values, except those for the vanadium compounds, are taken from Richards' Metallurgical Calculations: Vol. I, pp. 15-25.

It is known that elements like silver, copper and nickel are very easily deposited from their salt solutions. The heats of formation of the oxides of these elements are comparatively low, therefore the reducing power at the cathode necessary to decompose the salts is high enough to give the metal.

As the heat of formation of the oxides increases, more difficulty is encountered in obtaining metallic cathode deposits on electrolysis of the corresponding aqueous salt solutions. Such is the case with the oxides of tin, zinc, manganese and iron. With such oxides as aluminium oxide, deposits from aqueous salt solutions are practically unknown. It is therefore possible that, with vanadic oxide (V_2O_5) having a heat of formation greater than 441,000 gram calories, the reducing effect produced at the cathode by the electric current is insufficient to furnish the energy required to decompose a vanadic salt in aqueous solutions, which in general is greater for the salts than for that needed to decompose the oxides.

In some instances, too, elements are both acid and basic in their behavior. This is to some extent the case with tin and zinc, but

much more so for manganese, aluminium and vanadium. These latter elements form manganates, aluminates and vanadates very readily. As the tendency to form these compounds increases, so does the possibility to form a metallic cathode product decrease, while the tendency to form anode products from neutral or alkaline electrolytes increases.

It is obvious that with the element vanadium one is not likely to obtain the metal as cathode deposit from aqueous salt solutions, due to the high heats of formation of the salts and to the great tendency shown by this element to form vanadates.

I wish to express my profound gratitude to all the members of the Department of Metallurgy, for the kind advice, instruction and help rendered me in my work; and especially to Dr. Eduard F. Kern, under whom the research was conducted, for his invaluable suggestions and criticisms, which were a constant incentive.

OTHER PAPERS BY THE AUTHOR.

"The Concentration of Carnotite Ores and Some Similar Ores." Met. & Chem. Eng., Vol. X, pp. 356-359.

"The Extraction of Vanadium from Carnotite Concentrates." Met. & Chem. Eng., Vol. X, pp. 469-471.

"The Carnotite Industry." Trans. Am. Electrochem. Soc., Vol. XIV, pp. 361-375.

Columbia University,
New York City.

DISCUSSION.

W. R. Mott: This paper is very interesting and represents much careful work. The conclusion is that vanadium cannot be plated from aqueous solutions. This is entirely consistent (as noted in the paper) with the great energy required to decompose vanadium compounds. The heat of formation of vanadium trioxide is almost as great as that of aluminum trioxide. Some years ago I tried to secure electro-deposition of aluminum from scores of aqueous aluminum solutions, but had no success. I

suggest that the ethyl bromide solution found suitable for aluminum deposition by Dr. Patten might possibly be duplicated with vanadium. (See Transactions of this Soc., **5**, 177.) The organic solutions of vanadium fluorides might be worth trying.

It is really an important matter to deposit vanadium, because of its extreme hardness, high polish and resistance to corrosion.

In order that a clearer idea may be had of the intensity of the energy, it is well to reduce heats of formation to Faraday's Law of electrochemical equivalents. This has been done in the following table, which refers to the energy of union for one-half atom (one chemical equivalent) of oxygen and one atom of chlorine.

Heat of formation for ½ atom oxygen.		Heat of formation for 1 atom chlorine.	
ThO_2	81,500	$ThCl_4$	75,000
MgO	71,700	$MgCl_2$	75,500
Al_2O_3	63,400	$AlCl_3$	53,600
V_2O_3	58,800	VCl_3	62,300
MnO	45,400	$MnCl_2$	56,300
ZnO	42,500	$ZnCl_2$	48,600

In the above table the data of Ruff and Friedrich (Zeit. für anorg. Chemie (1914) **89**, 279, is used for vanadium trichloride, which has a greater heat of formation than even aluminum trichloride. Possibly if the heats of solution were also incorporated, the results might favor aluminum. In any case these results indicate that over a half volt more would be required to plate out vanadium than zinc. Zinc has nearly the highest decomposition voltage of any metal that it is practical to plate out of aqueous solution. Again zinc is favored by a high overvoltage of hydrogen, whereas vanadium would probably have a low overvoltage of hydrogen because of the high melting point of vanadium and its marked power of forming hydride.

Theoretically, vanadium deposition from aqueous solution is rather unpromising.

W. E. Koerner: The chemical properties of vanadium and tungsten are quite similar, and since I have done considerable work upon the latter, a brief statement of my tests may throw some further light on this discussion.

E. M. F. measurements of tungsten in normal solution of bases, acids and salts were made with auxiliary normal half cells, and

the single potentials of tungsten against these solutions were calculated from the values of E. M. F. obtained. The values of the single potentials were reduced to the standard Nernst hydrogen electrode.

These values are:

KCN	—0.656 V.
KOH	—0.315 V.
NH_4OH	—0.238 V.
$H2SO_4$	+0.193 V.
HCl	+0.256 V.
HNO_3	+0.311 V.
KF	+0.522 V.
KCl	+0.563 V.
KBr	+0.589 V.
KI	+0.733 V.

From calculated E. P. values we find that the E. P. varies with the nature of the electrolyte. In solutions of bases the metal is negative to the electrolyte, while in acid and salt solutions the metal is positive to the electrolyte.

The solution tension or solubility of a metal in an electrolyte is a function of the E. P. We can then say that the solubility of tungsten is greatest in solutions of bases and least in solutions of salts. Tungsten is more soluble in KCN than in KOH and more soluble in KOH than in NH_4OH. It is more soluble in H_2SO_4 than in HCl, and more soluble in HCl than in HNO_3. The order of solubility in salts is KF, KCl, KBr, KI.

Normal solutions of H_2SO_4, HCl and HNO_3 were saturated with $W(OH)_6$ by electrolyzing the acids at low current densities between tungsten electrodes. E. M. F. measurements were then made between half-cells, one member of which was tungsten in a normal solution of acid and the other member was tungsten in the saturated solution of $W(OH)_6$. These combinations were concentration cells, the concentration of $W(OH)_6$ in one case being zero.

The E. M. F. values obtained were:

$$\overset{+}{W} \mid \left\{ \begin{matrix} H_2SO_4 \\ W(OH)_6 \end{matrix} \right\} \mid H_2SO_4 \mid \overset{-}{W} + 0.117 \text{ V.}$$

$$\overset{+}{W} \mid \left\{ \begin{matrix} HCl \\ W(OH)_6 \end{matrix} \right\} \mid HCl \mid \overset{-}{W} + 0.057 \text{ V.}$$

$$\overset{+}{W} \mid \left\{ \begin{matrix} HNO_3 \\ W(OH)_6 \end{matrix} \right\} \mid HNO_3 \mid \overset{-}{W} + 0.009 \text{ V.}$$

From these values, we conclude that W $(OH)_6$ is most soluble in H_2SO_4 and least soluble in HNO_3. It is dissolved as a true solution and not as a colloid. The tungsten occurs in the cation.

Anodic Behavior of Tungsten: Tungsten dissolves anodically in aqueous solutions of ammonium hydroxide, hydroxlyamine, methyl ammonium hydroxides, methyl ammonium hydroxides, and propyl ammonium hydroxides to form the respective para-tungstates. At very high current densities the tungsten becomes passive. Tungsten also dissolves anodically in aqueous solution of potassium and sodium hydroxides to form the respective ortho-tungstates, becoming passive at very high current densities. Tungsten dissolves in *non-aqueous* solutions of HCl, hiCl, NaCl, KF, etc., with the formation of the respective halogen salts without becoming passive. Tungsten dissolves to a slight extent in *aqueous* solutions of HCl, H_2SO_4, HNO_3, KF, KCl, KBr, KI, with the formation of W $(OH)_6$, but the metal becomes passive. The metal stays active only at very low current densities.

The passivity of tungsten is due to oxide films, ranging in color from brown, blue and green to yellow. The colors are pronounced and can be followed as the electrolysis proceeds. The films are independent of the dissolved cation or anion. They are due to the OH ions reacting with the W.

The passivity is a function of the color of the film, the color varying with the amount of oxygen present. The passivity varies directly with the current, time and temperature, and inversely with the solubility of the film, the volume of electrolyte and the diffusion velocity. If the film dissolves as rapidly or more rapidly than it is formed, the tungsten will remain active.

The films can be dissolved and the passivity destroyed. Solutions of KOH and NH_4OH render passive tungsten active. Solutions of acids and salts make passive tungsten active if allowed to react for some time on it. Passive tungsten has been made active over night in distilled water.

In conjunction with the anodic solution of tungsten, the electrochemical equivalent was determined. Tungsten dissolves hexavalently in a solution of NH_4OH with 100 percent efficiency. From the loss in weight of a tungsten anode in NH_4OH and the coulombs of current, the electrochemical equivalent was found to

be 0.3173 mg. per coulomb. The theoretical value is 0.3175 mg. per coulomb.

Voltaic Cells: The single potentials of tungsten show that tungsten is negative to solutions of bases. Combining with tungsten in an alkaline solution a metal positive to the solution, we have a voltaic cell. Mercury and silver are positive to solutions of NaOH. The single potential of mercury in normal NaOH saturated with HgO is + 0.168 V. (H zero), while the single potential of silver in normal NaOH saturated with Ag_2O is + 0.378 V. (H zero). The E. P. of a special form of tungsten in normal NaOH is — 0.704 V. (H zero).

A cell composed of tungsten and mercury in normal NaOH saturated with HgO gives an E. M. F. of + 0.872 V., the mercury being positive. A cell composed of tungsten and silver in normal NaOH saturated with Ag_2O gives + 1.082 V., the silver being positive. By increasing the concentration of the NaOH to 10 N. in the W-Hg combination the E. M. F. is increased to 1.050 V. The cells are still in the experimental stage.

Standard Cells: Attempts are being made to use the above cell as a standard cell. Other cells, tried as standard cells, have combinations of tungsten and its compounds, with other metals. Some of these are:

$$\overset{+}{Hg} \mid Hg_6W_7O_{24} \mid Na_6W_7O_{24} \mid \overset{-}{W} + 0.552 \text{ V.}$$

$$\overset{+}{Cu} \mid Cu_3W_7O_{24} \mid Na_6W_7O_{24} \mid \overset{-}{W} + 0.395 \text{ V.}$$

$$\overset{-}{Cd} \mid Cd_3W_7O_{24} \mid Na_6W_7O_{24} \mid \overset{+}{W} + 0.434 \text{ V.}$$

These cells are also still under investigation.

Tungsten Storage Battery: At present we have under investigation cells made with combinations of tungsten and tungsten oxides. The first, *A,* had, before charging tungsten and tungstic acid as the positive electrode, and tungsten as the negative electrode. H_2SO_4 1.4 was employed at both electrodes. No change in color was observed. An E. M. F. of 0.08 volt was observed before charging. The E. M. F. immediately after charging was 3.00 volts, 24 hours after charging the E. M. F. had dropped to 0.2 V.

The second, *B,* had, before charging, tungsten and tungstic acid,

as both positive and negative electrodes. During charging gas was evolved at the positive electrode. The yellow color of the negative electrode changed to blue-black. The positive electrode remained unchanged. Before charging no E. M. F. was observed. Immediately after charging, an E. M. F. of 3.2 V. was observed. This value dropped to + 0.55 after the cell had stood for 24 hours.

The third and best combination tried had, before charging, tungsten as positive electrode and tungsten and tungstic acid as negative electrode. During charging the yellow tungsten acid was reduced through a series of colored oxides to a blue-black compound, probably W_2O_5. The tungsten of the positive electrode became covered with a brown film, presumably WO_2.

Before charging an E. M. F. of — 0.08 V. was observed. Immediately after charging the E. M. F. was as high as 6.20 V. This value was not stable, 24 hours after charging 0.75 was obtained. This value has remained constant for two weeks.

With a small, poorly constructed cell, we were able to light a 2.7 V. 2 C. P. battery lamp with current produced from the storage cell immediately after charging. The cells are still in the experimental stage. Further work will be done and further reports made to this Society.

C. G. Fink: I should like to emphasize a number of points that Mr. Koerner brought out. First of all, the relative solution tension of tungsten in acids and alkalies. We get a decidedly higher electro-motive force value with alkalies than with acids.

Another point is the passivity of tungsten. Tungsten, like iron, grows passive in nitric acid; but tungsten loses its passivity very rapidly upon immersion in alkali solutions, whereas iron does not.

As regards the tungsten storage cell, owing to the fact that tungsten can be obtained as a very fine wire with a very big surface, wire much thinner and stronger than you can obtain in case of lead, it may be that we can eventually build up a storage battery which will be more efficient than our lead storage battery, and lighter than that one, even though the specific gravity of tungsten is higher than that of lead.

F. C. Frary (*In part communicated*): It appears certain that the author has confused the solution-tension of tungsten with its solubility in certain reagents. The measurements of single poten-

tials give us the force with which the element sends (or tends to send) its ions in solution, and this force is a function of the heat of formation of the resulting compound plus its heat of solution at the concentration used. This may be relatively large, while the actual solubility, or amount per unit volume in the saturated solution, may be either small or large, depending upon other factors. We need to be extremely careful in our use of technical terms in order to prevent such errors as this. I hope the author will take occasion to correct this before publication.

W. E. Koerner: This electro-motive force 0.117 V. in the combination

$$W \mid \left\{ \begin{matrix} H_2SO_4 \\ W(OH)_6 \end{matrix} \right\} \mid H_2SO_4 \mid W$$

is due to the dissolved tungsten hexahydroxide. This is ionized. In the combination

$$W \mid \left\{ \begin{matrix} HNO_3 \\ W(OH)_6 \end{matrix} \right\} \mid HNO_3 \mid W$$

the solubility is low and we have small electro-motive force. If we had no $W(OH)_6$ dissolved the combination W | acid | W would give no electro-motive force value at all.

William Blum: The attempt to deposit vanadium metal directly is of interest in connection with the fact that up to a short time ago a number of electrotypers used nickel solutions, to which had been added a few ounces of vanadium chloride to a hundred gallons of solution. They had gotten an idea that since vanadium increased the hardness of steel, it would increase the hardness of their nickel deposits (commonly called "steel"). It took a few analyses to show that a short time after they added the vanadium salt to the neutral nickel solution the vanadium was resting quietly in the slime at the bottom of the tank, so that none ever got to the cathodes.

S. Fischer (*Communicated*): In answering Mr. Mott's discussion, when the straight methyl and ethyl vanadium salts were investigated without satisfactory results it was deemed unnecessary to try the ethyl bromide compounds of vanadium. It would, however, undoubtedly add to the completeness of the work, if

electrolysis of the ethyl bromide solution of vanadic oxide were investigated. There are two reasons why a deposition even from an ethyl bromide solution would be unlikely to occur; first, vanadium, unlike aluminum, forms several oxides, thus making the molecular structure of the vanadium compound much more complex than that of the corresponding aluminum compound. I am thoroughly convinced from the results obtained in the course of much electrolytic work, that the more possible valencies a metallic element possesses, the greater is the difficulty of obtaining a metallic cathode deposit. Omitting complex and double salts, that salt is most suitable for electrolysis which contains the metallic element in the most stable form of valency.

Secondly, as mentioned in my article, Mixter's determinations of the heats of formation of the vanadium oxides are merely approximations. Considering all the factors known, such as the greater difficulty of depositing metallic vanadium from a fused electrolyte of the double sodium or calcium and vanadium fluoride as compared with the deposition of aluminium from a similar electrolyte, and the higher heat of formation of the vanadyl chloride as compared with that of the aluminium chloride, it would seem that at least the heat of formation of the V_2O_3 as given by Mixter is too low.

The conclusion drawn from the above is that of two elements having high heats of formation for their oxides, the one having the least number of possible valencies will be more apt to give a metallic cathode deposit on electrolysis of an aqueous salt solution. Taking this into consideration, it would seem improbable to obtain a metallic deposit from a vanadium ethyl bromide electrolyte.

A paper presented at the Thirtieth General Meeting of the American Electrochemical Society, held in New York City, September 28, 1916, Mr. L. E. Saunders in the Chair.

ELECTROLYTIC ZINC DUST.[1]

By Harry J. Morgan and Oliver C. Ralston.[2]

The sudden increase in the price of zinc dust after the beginning of the European war, owing to the cutting off of the German and Belgian supply, led to the conducting of some experiments on the possibility of its production on a commercial scale from solutions of zinc, and the substitution of the zinc made in this manner for the zinc dust ordinarily used in the precipitation of gold and silver in the cyanide process.

As the Salt Lake City station of the U. S. Bureau of Mines, in co-operation with the Department of Metallurgical Research of the University of Utah, is carrying on investigations that have for their object the treatment of low-grade and complex zinc and lead ores or products, it was thought well to determine whether the zinc contained in such ores and products could not be utilized in the manner above indicated, and so supply the demand which had arisen for zinc dust.

The United States, in 1913, imported 4,382,470 lb. of zinc dust, valued at $227,585. Most of this was from either Germany or Belgium. The domestic production, in comparison with the imports, was very small. In the years 1912 and 1913 the domestic production was 492 and 423 tons respectively, while the imports were 2,400 and 2,200 tons respectively. For a time the zinc dust made in zinc smelters was a drug on the market and when first utilized in cyanidation could be bought for a lower price per pound than solid zinc. After the advantages of the use of zinc dust for precipitation were realized, so much zinc dust began to be used for this purpose that it brought a premium of about 3 cents per pound over what the value of spelter was at the beginning of the war. Since that time its price has averaged about

[1] By permission of the Director, U. S. Bureau of Mines. Communicated by D. A. Lyon, Metallurgist in Charge of Salt Lake Station of Bureau of Mines.

[2] H. J. Morgan, Research Fellow, Univ. of Utah; O. C. Ralston, Asst. Metallurgist, U. S. Bureau of Mines.

30 cents per lb., without much fluctuation. Some American zinc smelters have undertaken to supply the demand but their product has never been equal to the German zinc dust.

Some attempts by Morgan,[3] were made in the application of a jet of air to atomize a column of molten zinc for making zinc dust. This work was carried on at the Bureau of Mines Exhibit at the San Francisco Exposition, but the zinc dust was not satisfactory for cyanide precipitation. While it was fine enough to pass a 200-mesh screen, it was only 25 percent efficient in the precipitation of silver from cyanide solutions and a microscopic examination showed that the small pellets of zinc were in the shape of congealed droplets which present a minimum of surface for reaction with the silver cyanide solution. This idea has been further carried out at Anaconda and we are informed that 10 to 15 tons of atomized zinc is now being prepared per day, in preference to sponge zinc made by electrolytic deposition from sulphate solutions. This dust is being used for purification of zinc sulphate solutions, for the reason that the more finely divided electrolytic sponge tended to clog up the Schriver filter presses used at that plant.

To us, a better idea seems to be the making of a zinc sponge by electrolytic methods, the sponge to be of such a nature that it would crumble to dust when dried. The variety of electrolytic conditions available, with the different electrolytes which can be used, and the resulting great differences in the physical properties of the precipitated metal, gave promise of the possibility of a zinc dust which would be highly efficient and rapid. As a result of the experimental work, which has been carried on, it is believed that this possibility has been realized. In addition to its use for precipitating gold and silver from cyanide solutions, zinc dust can also be used in sherardizing, and for chemical purposes, such as reduction of organic compounds, etc. Sherardizing requires a considerable proportion of relatively coarse particles of zinc, similar to the atomized zinc above mentioned, but it is possible that the manufacture of dyes and other such chemicals in the United States can create a considerable demand for electrolytically prepared zinc dust of high purity and efficiency. The following

[3] In this work Morgan was assisted by Dr. R. H. Bradford, Professor of Metallurgy, of the University of Utah, and under the direction of G. H. Clevenger, Professor of Metallurgy at Stanford University.

work was carried on with a view to preparing a zinc dust satisfactory for cyanide practice and does not consider the needs of the sherardizing industry, or of the chemical industries.

According to Sharwood,[4] zinc dust for use in cyanide precipitation should be fine enough so that 90 percent of it will pass 200 mesh and it must be high in metallic zinc. A considerable amount of zinc oxide may be present without seriously affecting the efficiency of precipitation by the metallic zinc. The following method of testing the efficiency of precipitation by zinc dust is given by Sharwood: After passing the dust through a 100-mesh screen to break up the lumps, 303 milligrams are weighed out and added to 250 cc. of 1 percent silver cyanide solution which contains 0.15 percent free cyanide. The solution is stirred occasionally for two hours, after which it is withdrawn from the precipitated silver by filtration. The precipitated silver is dissolved in nitric acid and titrated with ammonium sulpho-cyanate, using a ferric salt as an indicator; or else the precipitated silver is scorified and cupelled to be weighed. Each milligram of silver precipitated represents 0.1 percent efficiency of precipitation. This test is merely an empirical one of general acceptance which is admittedly near enough to allow of intelligent buying of zinc dust. It is stated by Herz[5] that the efficiency of zinc dust should be over 40 percent and that dust with less than 30 percent efficiency generally gives poor results. Dust of over 50 percent efficiency is hard to obtain. The average grade of zinc dust from Europe is 45 percent efficient but in this work we have been able to get dust giving an efficiency of 74 percent.

The usual endeavor of the zinc hydro-electro-metallurgist is to obtain solid reguline deposits of zinc rather than the sponge, as the sponge metal can rarely be melted down into spelter. The literature on electrolytic zinc is full of instances where work along certain lines was stopped on account of the "tendency" of the zinc to be deposited in a spongy form. However, we found that in duplicating this work and following the conditions as given, that there is only a *tendency* and that the average result of such conditions is trees, warts, or loose crystalline zinc. We found as much difficulty in obtaining a true sponge as the beginner usually

[4] J. Chem. Met. Min. Soc., So. Africa, **7**, 332 (1912).
[5] Tr. Am. Inst. Min. Eng., **52**, 144 (1915).

finds in getting smooth solid deposits. Conditions of high current density and low current density, high acidity and low acidity, or basicity, high temperature, etc., were tested and it was very hard to get all the sponge that others had reported as being so easily obtained.

The writers have been informed that one metallurgical company produced several thousand pounds of zinc dust at their electrolytic zinc plant in Welland, Ontario, by allowing the temperature of their solutions to go up above 70° C. and that it was used by one of the local firms with indifferent success. The electrolytic plant in question is operating a sulphate solution of zinc in which ore is suspended in the solution while the cathodes are protected by bags. Most of the sponge or the loose crystals prepared by us from sulphate solutions did not possess a very high precipitating efficiency. Spongy zinc was formed when solutions of zinc sulphate containing dissolved zinc oxide were used, but as soon as the solutions became acid, due to the formation of sulphuric acid at the anode, the zinc lost most of its spongy characteristics. An excess of zinc oxide suspended in an open cell is not desirable, as it mixes with much of the loose zinc sponge formed. Removal of the solution to an outside vat, for treatment with zinc oxide, is not desirable on account of the slow, and low solubility of the zinc oxide in the zinc sulphate solutions.

The method of adding impurities to the solution was resorted to in order to get spongy zinc. Copper and arsenic were found to be most efficient for this purpose, but copper is not a desirable constituent in zinc dust on account of its presence in the precipitate of the precious metals. Arsenic is also undesirable in the precipitate, if the latter is to be treated with sulphuric acid before melting into bullion, due to the formation of poisonous arsine. All the copper was found to be deposited quite quickly from solution with the sponge zinc, but after the deposition of the copper, the zinc deposits began to be more solid and crystalline. A continual drip of copper sulphate into the electrolytic vat is hence necessary. The addition of iron as an impurity did not result in producing successful sponge zinc. Furthermore, the oxidation and reduction of iron salts at the electrodes lowers the current efficiency.

The favorable results obtained in solutions made slightly basic encouraged the use of basic solutions of zinc, such as sodium zincate. The zincates allowed a wider latitude in the precipitation of zinc sponge than any other solutions tested. Lead anodes tend to dissolve, and zinc anodes dissolve almost quantitatively. Iron anodes are practically unaffected, especially those made of the better grades of iron. After doing this work it was discovered that practically the same idea had been patented by Sherard Cowper-Coles in British patent 13,977 of 1907. The electrical conditions best for this work are not mentioned by him, but we find that a wide range of voltages are allowable, and most of our work has been done at a current density of about 300 amp. per sq. ft. (3225 amp. per sq. m.). Cowper-Coles mentions the possibility of using galvanized "hard zinc" for anodes when making sponge zinc, as the iron is not dissolved, while the zinc is, thus lowering the operating voltage and replenishing the solution. He also recommends the use of a rotating vertical disc for a cathode, a form of cathode which we had adopted after some considerable test work. The disc can be made of iron and the upper half projects out of the electrolyte. The sponge is scraped off the disc into water as the disc slowly revolves. Rapid rotation of this disc is not allowable, as the better agitation of the electrolyte causes the formation of adherent zinc which defeats our purpose. To have a barely perceptible motion of the disc is sufficient. We had anticipated trouble in the drying of the dust, but met with none, as we found it could be heated to 250° C. on the hot plate in the open air without ignition. The washing of the sponge free from the adhering solution of sodium zincate must be performed with weaker caustic, as the zincate hydrolyses in water solution to zinc hydrate and sodium hydrate. A water wash can follow a caustic soda wash. The dust prepared in this manner was highly efficient (over 70 percent).

The data, obtained as a result of some of the tests performed, are summarized below:

Test 1. 50 percent $ZnSO_4.7H_2O$ solution at 60° C.; lead anode; iron cathode; current densities, 1 to 15 amp. per sq. ft. (11 to 162 amp. per sq. m.). Warty deposit. At boiling temperature a crystalline warty deposit is obtained.

Test 2. 10 percent Zn and 1 percent ferrous iron in sulphate solution. Current density 15 amp. per sq. ft. (162 amp. per sq. m.) ; voltage, 3.5. Deposit warty to loosely crystalline. Improves slightly on raising current density to 245 amp. per sq. ft. (2633 amp. per sq. m.),

Test 3. Neutral solutions of $ZnSO_4.7H_2O$, 15 percent. Current densities of 8 to 15 amp. per sq. ft. (86 to 162 amp. per sq. m.). A small amount of ZnO added. Anode of zinc. Result, a fair sponge.

No. 1. Fairly coarse material; precipitation efficiency.....68.6%
No. 2. Fine material; precipitation efficiency.....70.1%
No. 3. Coarse material; precipitation efficiency.....64.9%
No. 4. Coarse material; precipitation efficiency.....65.6%

Test 4. Neutral solution of zinc sulphate like above, 3 percent Zn. The electrolysis was continued until the acidity increased to a point where the zinc became platy and coarsely crystalline. The precipitation efficiency of the zinc was 65 percent.

Test 5. 20 percent zinc chloride solution containing dissolved ZnO. Current density 500 amp. per sq. ft. (5375 amp. per sq. m.). Two successive samples of sponge taken. Efficiency of first test 60 percent, of the second, 45 percent. The sponge prepared from this solution showed a strong tendency to oxidize on drying.

Test 6. Solution of zinc sulphate, containing 5 percent Zn and 2 percent sulphuric acid. Anode of "galvanizers dross." After most of the acid had been used up (during which time a fairly good smooth deposit of zinc was obtained) the deposit became spongy and the dust gave a precipitation efficiency of 56 percent.

Test 7. Sodium zincate solution. 25 percent caustic, 6 percent Zn. Carbon anode. Iron cathode. Electrolyzed down to solution of 2.5 percent Zn. Three periods of 15 minutes, during which the zinc sponge of each period was collected separately.

No.	Voltage	Current Density	Current Efficiency	Ppt. Efficiency
1	4.7	260 amps. sq. ft.	83.0%	60.5%
2	4.6	270 " "	85.4	57.0
3	4.7	250 " "	69.2	56.0

Test 8. Sodium zincate solution: 22 percent NaOH, 6 percent Zn. Iron anode and cathode, reduced in 15 minutes to 5 percent

Zn. 4.6 volts. Current efficiency 90.7 percent and precipitation efficiency of sponge, 65.5 percent.

Test 9. Sodium zincate solution: 25 percent NaOH; 6.5 percent Zn at beginning and 1.5 percent at end of test. Lead anode, iron cathode. Lead anode slowly dissolved, and solution became more caustic, necessitating the addition of more zinc oxide. Three periods in test, the second starting when strong alkalinity developed.

No.	Zn.	Pb.	Eff. Pptn.
1	94.5%	4.5%	55.5%
2	79.5	16.6	39.6
3	68.5	23.6	34.7

Test 10. Sodium zincate solution as in test 8. Disc cathode rotation barely perceptible. Sponge of 70 percent precipitation efficiency.

Test 11. Sodium zincate solution. 8.9 percent Zn at beginning and end of electrolysis. Iron disc cathode. Zinc anode. 330 amp. sq. ft. (3548 amp. per sq. m.) 4.5 volts. Current efficiency, 54.2 percent. Precipitation efficiency of dust 74.5 percent. Analysis of dust shows 97.5 percent Zn.

Test 12. Sodium zincate solution 30 percent NaOH, 8.9 percent Zn at beginning and 3.46 percent Zn at end of five hours electrolysis at 5 volts. The electric current efficiency was determined at short intervals as follows:

Time, Min.	Current Eff.	Precip. Eff.
30	58%	74%
60	71	..
90	60	..
120	50	..
180	66	..
240	62	..
300	53	74.2

The dust on analysis showed 97.5 percent Zn. The average current efficiency in the deposition of the zinc was about 60 percent, and one pound of dust requires somewhat less than 3 K. W. hours.

From test 12 it can be seen that the best zinc dust was prepared from a solution containing about 30 percent of caustic soda and saturated with zinc oxide. A high current density, with the corresponding temperature, seems to be the best conditions for ob-

taining highly efficient zinc dust. This causes a higher electric energy consumption than one might wish, but the figure of 3 K. W. hours per lb. (6.6 K. W. H. per kg.) of zinc dust is very safe in being high.

Test 9 shows the effect of the addition of lead to the zinc dust. It can be seen that the presence of much lead in the zinc dust is certainly undesirable. Zinc shavings are often given a bath of lead acetate in order to form a zinc lead couple which will be more efficient in precipitation of the precious metals. We do not know whether the lead deposited with the zinc in these tests was in the proper physical condition to allow the setting up of an electrical couple, as the appearance of the zinc dust did not give any indication of its physical condition. At any rate, over 4 percent Pb in the zinc dust prepared by this method would seem to be detrimental to efficient precipitation. The lead anode undoubtedly dissolves as the plumbite, which is known to be soluble in caustic alkali. In case it were ever found to be desirable to have a small amount of lead in the electrolytically deposited zinc, a small auxiliary lead anode could be used of sufficient area to give the desired percentage of lead in the zinc dust.

Test 11 shows that a zinc anode can be used in order to keep the solution approximately constant in composition. In this case the arrangement serves only as a medium for transforming spelter into zinc dust. This point is of importance, as it should allow the manufacture of zinc dust at each mill from the spelter usually bought for turning into zinc shavings. It is possible that the zinc smelters could be induced to cast the zinc into anodes instead of the regular bars. It was somewhat of a surprise, however, to find no decrease in voltage where a soluble anode was used, as compared to an insoluble anode. This is possibly due to the extraordinarily high current density used.

Care of Zincate Solutions. Some question arises as to the best way to utilize the zincate solutions in preparing zinc dust. It might be possible to treat roasted zinc ores or naturally oxidized ores, with a solution of caustic alkali, leaching out the zinc as a zincate. It would also be possible to prepare the zincate from zinc oxide, purchased on the market. Since iron in the zinc oxide does not affect the properties of the zinc sponge, it might be pos-

sible to keep the solution up to strength by the addition of zinc oxide which is too contaminated with iron oxide to pass as a pigment.

The caustic solution takes up carbon dioxide from the air forming sodium carbonate. On account of the strong solution of caustic required there is some question as to the recausticizing of this solution by lime. According to Lunge[6] the speed of the reaction between sodium carbonate and quicklime depends upon the temperature. Equilibrium is reached in 2 to 3 hours at 108° C., in 12 hours at 80° C. and more than 40 hours at 62° C. Further, in 20 percent caustic solution the reaction comes to an equilibrium at 90 percent completion, leaving some undecomposed carbonates in the solution. How serious this point is liable to be in practice we are unable to say, as our solutions, which were worked in some instances, for a number of weeks, did not show signs of fouling.

In testing the leaching of several oxidized ores with caustic soda solutions it was found that it was very hard to get extractions of as much as 50 percent, either by treating calcined or raw oxidized ores. It is known that ignition renders zinc oxide more difficult of solution in the caustic but the average raw zinc "carbonate" ore will not allow of more than about 30 percent extraction of the zinc, while a calcined sample in this instance gave as high as 50 percent extraction. Anyway it is probable that the carbon dioxide from a zinc carbonate ore would tend toward speedy fouling of the electrolyte. Hence we do not consider as practical the proposition to make up the solutions from "carbonate" ores.

In case a spelter anode is used the question of preparation of the solution assumes small importance and the only serious difficulty to be considered is that of fouling the solution with carbon dioxide, taken up from the air. So far as our work is concerned, this is still a problem.

Costs. Due to the high consumption of electrical energy, 3 K. W. H. per lb. (6.6 K. W. H. per kg.) of zinc dust, the principal item to be considered is the cost of electric energy. The high efficiency of the zinc dust in comparison with ordinary zinc dust and the high efficiency of the latter in comparison with zinc

[6] Lunge: Sulphuric Acid and Alkali, vol. 2, 806.

shavings precipitation, will probably allow of considerably higher cost per pound for the new dust than for zinc shavings, or ordinary commercial zinc dust.

The high current density used allows of smaller electrolytic tank equipment than is used in most electrolytic installations. The design of a small set capable of supplying the ordinary small cyanide mill with zinc dust is hence a matter of interest. We believe that the figures presented allow of the design of such plants, but until a semi-commercial plant has been built and tested out thoroughly it is needless to present possible designs. The object of this work, as likewise of other investigation which has been conducted by the Salt Lake station of the Bureau and the Department of Metallurgical Research of the University of Utah, has been to test out various ideas and suggestions with a view of determining whether or not they possess sufficient merit to warrant their being tried out on a semi-commercial or commercial scale.

CONCLUSIONS.

1. By depositing a "sponge" metal from solutions by electrolysis it is possible to get a zinc product that on drying crumbles into "zinc dust."

2. Sponge metal can be obtained from zinc sulphate solutions by the continual addition of a small amount of either copper or arsenic salts to the electrolyte. The objection to the use of zinc dust prepared by this method is the needless dilution of the bullion caused by the copper, and the danger met in the handling of gold or silver precipitates when arsenic is used to produce the sponge. These difficulties are probably not insurmountable. Fairly impure solutions can be worked only when zinc sponge is desired, and this will not handicap the ordinary electrolytic methods.

3. The preparation of zinc sponge is also possible from sulphate solutions by keeping acidity low and temperature high. Zinc oxide, rendering the solution slightly basic, is the most desirable chemical for maintaining this condition. It is subject to the objection that it is only slowly and slightly soluble in zinc sulphate solutions.

4. The same remarks apply to zinc sponge prepared from chloride solutions, except that the zinc sponge seems to be more inclined to be oxidized during drying.

5. Sodium zincate solutions allow of the deposition of zinc sponge under a widely varying range of electrical and thermal conditions. Stirring of the electrolyte must be avoided. Current efficiencies of about 60 percent and zinc dust precipitating efficiencies of 70 to 75 percent are possible. There seems to be no difficulty in getting one pound of zinc dust from a solution of zinc, with 3 K. W. hours of energy.

6. Sodium zincate solution recommends itself because of its ease of preparation from caustic soda and zinc oxide, both of which are articles of commerce. The zinc tenor of the solution can be maintained either by the addition of more zinc oxide or by the use of zinc anodes, by which latter process spelter can be converted into zinc dust.

A paper presented at the Thirtieth General Meeting of the American Electrochemical Society, held in New York City, September 28, 1916, Mr. L. E. Saunders in the Chair.

THE ELECTROLYTIC RECOVERY OF LEAD FROM BRINE LEACHES[1]

By Clarence E. Sims[2] and Oliver C. Ralston.[3]

INTRODUCTION AND HISTORY.

The knowledge that lead sulphate and lead chloride are soluble in a strong brine solution and that lead may be recovered from such a brine solution by electrolysis is not new, although certainly not widespread. In fact, as long ago as 1854, M. M. Bequerel, of Paris, reported in Comptes rendus, **38**, 1095 (1854), of the work he had done on lead leaching and electrolysis. In all he treated about 20,000 lb. of ore, mostly from South American and Mexican sources. His method of procedure was to give the ore a sulphatizing roast in the presence of salt and leach out the lead sulphate and silver chloride with saturated brine. The brine was then electrolyzed to recover the metals. The principles of his process were quite similar to those of the process described in this paper. However, Bequerel could never have made his process commercially practical because of the then existing commercial conditions, which are much changed now. For instance, he obtained his current from the only source he knew of, namely the primary cell.

H. R. Ellis claims to have developed, in 1893, a process for leaching oxidized ores of lead with a hot (but not saturated) brine containing some copper sulphate. Mr. Theodore P. Holt, at the mill of the Mines Operating Co., at Park City, Utah, found that, on giving his ore a chloridizing roast and leaching with a 20 percent salt solution, lead built up in the brine to about 8 lb. (3.6 kg.) per ton of solution. At the Bunker Hill and Sullivan mill, at Kellogg, Idaho, a lead sulphide ore, which could not be

[1] Contributed by the Department of Metallurgical Research of the University of Utah, in co-operation with the U. S. Bureau of Mines. Published by permission of the Director of the U. S. Bureau of Mines.

[2] Fellow, Department of Metallurgical Research, University of Utah.

[3] Assist. Metallurgist, U. S. Bureau of Mines.

successfully concentrated, was given a chloridizing roast and leached with brine, with good results.

However, we believe that Neil C. Christensen was the first one, since Bequerel did his work, to conceive the idea of recovering lead from the brine by electrolysis. His work was done in the Knight-Christensen mill at Silver City, Utah. He had been rather successful in recovering lead in this manner on a laboratory scale, and was taking steps to enlarge his experimental plant, when the mill burned down.

The following work was carried out in the laboratories of the Department of Metallurgical Research of the University of Utah, in co-operation with the U. S. Bureau of Mines, and was undertaken for the purpose of finding a commercially feasible process for the recovery of the values contained in low-grade lead ores, which, for any reason, cannot be recovered by concentration processes of any kind.

METHOD OF EXPERIMENTAL PROCEDURE.

The Process. In order to take advantage of the fact that both the sulphate and the chloride of lead will dissolve in a saturated salt solution, carbonate ores of lead were treated with brines containing at least enough sulphuric acid to convert the lead to one of the soluble forms. The sulphide ores of lead were given a sulphate roast, which converted 75 to 99 percent of the lead to the sulphate form and the rest to the oxide form. Enough sulphuric acid was added to the brines to convert this oxide to a soluble form. These leaching solutions were electrolyzed to recover metallic lead. Various details covering the leaching of lead ores by the use of brines will be published later, the present paper being designed to present an exposition of the necessary conditions for recovering lead by electrolysis of the solutions.

Leaching. The leaching was done in two-liter acid bottles. Four bottles were used, eight liters of solution being required in all runs. The ore and brine were put together in the bottles with enough sulphuric acid to convert all of the lead to sulphate of lead. The bottles were then tightly stoppered and agitated on the rolls, usually from 2 to 5 hours, although at times leaches were allowed to run over night. When small amounts of CO_2

were formed, owing to the action of the acid, the stoppers were removed from time to time to relieve the gas pressure. But in ores containing large amounts of carbonate, just enough brine was put in with the ore so that the brine would not run out of the bottle when lying on its side unstoppered. Then acid was put in and the bottle later filled with saturated brine and put back on the rolls for leaching.

The filtering was done in an eight-inch Buchner funnel, using a water suction pump. After the pulp had been drained as thoroughly as possible by this means it was washed with barren brine

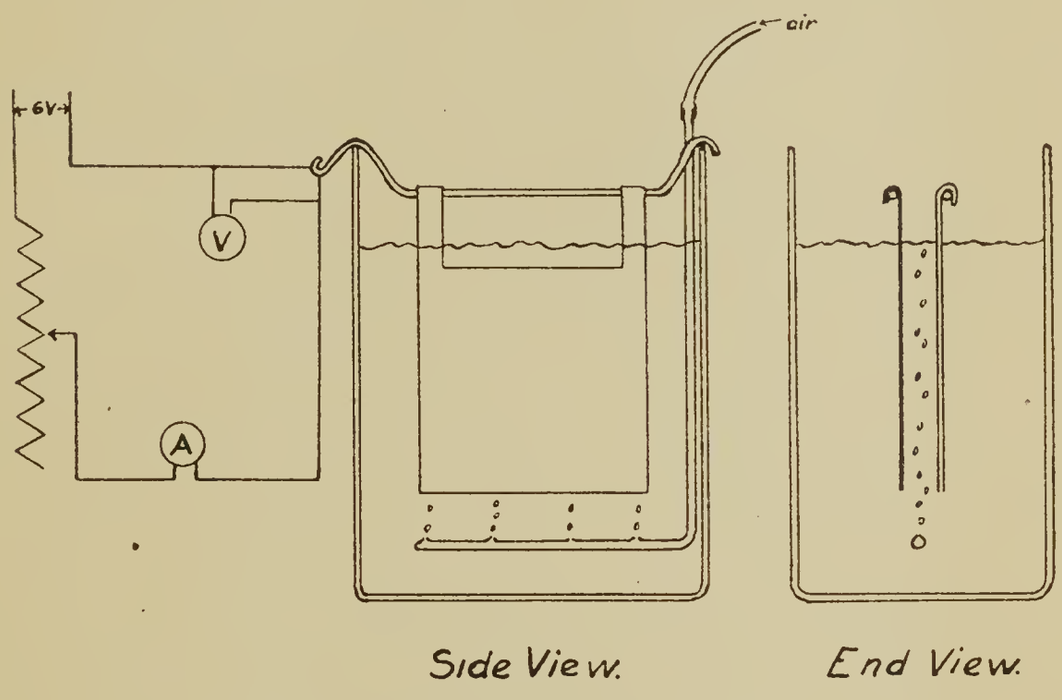


Fig 1. Experimental Electrolytic Cell.

and then with water. The wash with brine must be given first in order to prevent the re-precipitation of the lead in the ore, because the pregnant brine on being diluted with water precipitates lead chloride. The water wash is to recover the salt in the ore.

Electrolysis. The electrolysis was carried out in a 6.5 × 9 × 12 inch (15 × 23 ×30 cm.) storage battery jar which holds conveniently eight liters of electrolyte. The accompanying sketch shows the arrangement of the cell in detail. The electrodes were six inches square and were hung by strips over heavy copper wire bus-bars. The anode, except in the case of the insoluble anode, was of 1/16 in. (1.6 mm.) sheet iron and the cathode of ⅛ in.

(3.2 mm.) sheet lead. The cathode and anode were both soldered to the bus-bars to afford better connection. The insoluble anode was of ⅜ in. (9.6 mm.) carbon. Agitation and circulation of the solution was secured by means of compressed air which was bubbled up between the plates through holes in the glass tube shown in the sketch. A 0-3, 0-15, 0-30 Weston ammeter and a 0-3, 0-15, 0-150 Weston voltmeter were used for measurements, and a slide wire resistance to regulate the current. As a source of current, two batteries consisting of three 15-ampere storage cells, each, were available.

The lead was deposited as a sponge and was allowed to fall off of the cathode and collect in the bottom of the cell to be recovered later. The free evolution of hydrogen near the end of a run was taken as an indication that the solution was depleted of lead and electrolysis was stopped.

The sponge lead was collected by draining or filtering off the solution in a small Buchner funnel. While in the funnel it was washed several times, sometimes with hot water, and at times a little acid was added to the first wash. The sponge was then pressed to remove most of the water, after which it was quickly dried on the hot plate. In melting it down to solid lead it was placed in a fire-clay or iron crucible with a light cover of charcoal (to maintain a reducing atmosphere) and heated over a gas flame or in a muffle. Samples of the electrolyte were taken with a pipette while the electrolyte was being agitated. Lead analyses were run by the chromate method according to Low. Iron was determined by permanganate titration, both zinc and stannous chloride being used at different times for reduction. Zinc was determined by titration with ferrocyanide. Sulphur was determined gravimetrically by precipitation as barium sulphate.

As a rule, the production of sponge metal in the electrolysis of metal-bearing solutions is to be avoided, due to the fact that most metals, when in the form of sponge, are melted down into bars with great difficulty. It is almost an impossibility to melt down zinc sponge. In the case of the lead sponge, the lead not being an especially active metal, and having a low melting point and as its oxide is easily reduced, the difficulty anticipated did not materialize. In this way electrolysis is not handicapped by the attempt to form reguline deposits of lead.

EFFECT OF CYCLIC RUNS.

In starting the series of cyclic runs eight liters of saturated brine were used. After agitation with ore the brine was filtered off and was then electrolyzed until nearly depleted of lead. It was then run back onto fresh ore for another leach, thus completing one cycle. Enough fresh brine was added to each cycle to replace that lost by evaporation, etc., and to keep the volume of solution up to eight liters.

Iron builds up slowly in the solution with each cycle until it reaches the neighborhood of 1.5 percent when it seems to approach equilibrium. As an amount of iron equivalent to the amount of lead precipitated enters the solution during each electrolysis, then iron must also be thrown out of solution during each cycle. Analysis before and after a leach shows that it is left in the ore. As the leaching solution, although acid at the start, becomes neutral before the end of each agitation with ore, the iron is probably hydrolyzed to either the hydroxide or to a basic chloride. When the electrolysis of the solution has been completed, most of the iron is present as ferrous iron, and it is obviously only the ferric iron which is precipitated. However, it is possible in a neutral solution for the ferrous chloride to oxidize to a basic ferric chloride.

When zinc is present in soluble form in the ore, it goes into solution to a small extent. While zinc sulphate is known to be soluble up to at least 10 percent of zinc in brine solution, the zinc always remained below 1 percent in the tests above mentioned.

Sulphates build up slowly and steadily at first. The sulphur is, of course, present largely as sodium sulphate, formed by the double decomposition of the salt and the lead sulphate, when the latter goes into solution. Sodium sulphate is only slightly soluble in saturated brine, however, and readily crystallizes out when present in an amount equivalent to less than 1 percent of sulphur. Sodium sulphate is different from other impurities in that it is desirable in small amounts, due to the fact that it increases the solubility of lead sulphate in brine. The solution of salt and sodium sulphate, having the maximum solubility for lead, contains about 0.6 percent sulphur.

Aside from the effect of the sodium sulphate, the solubility of

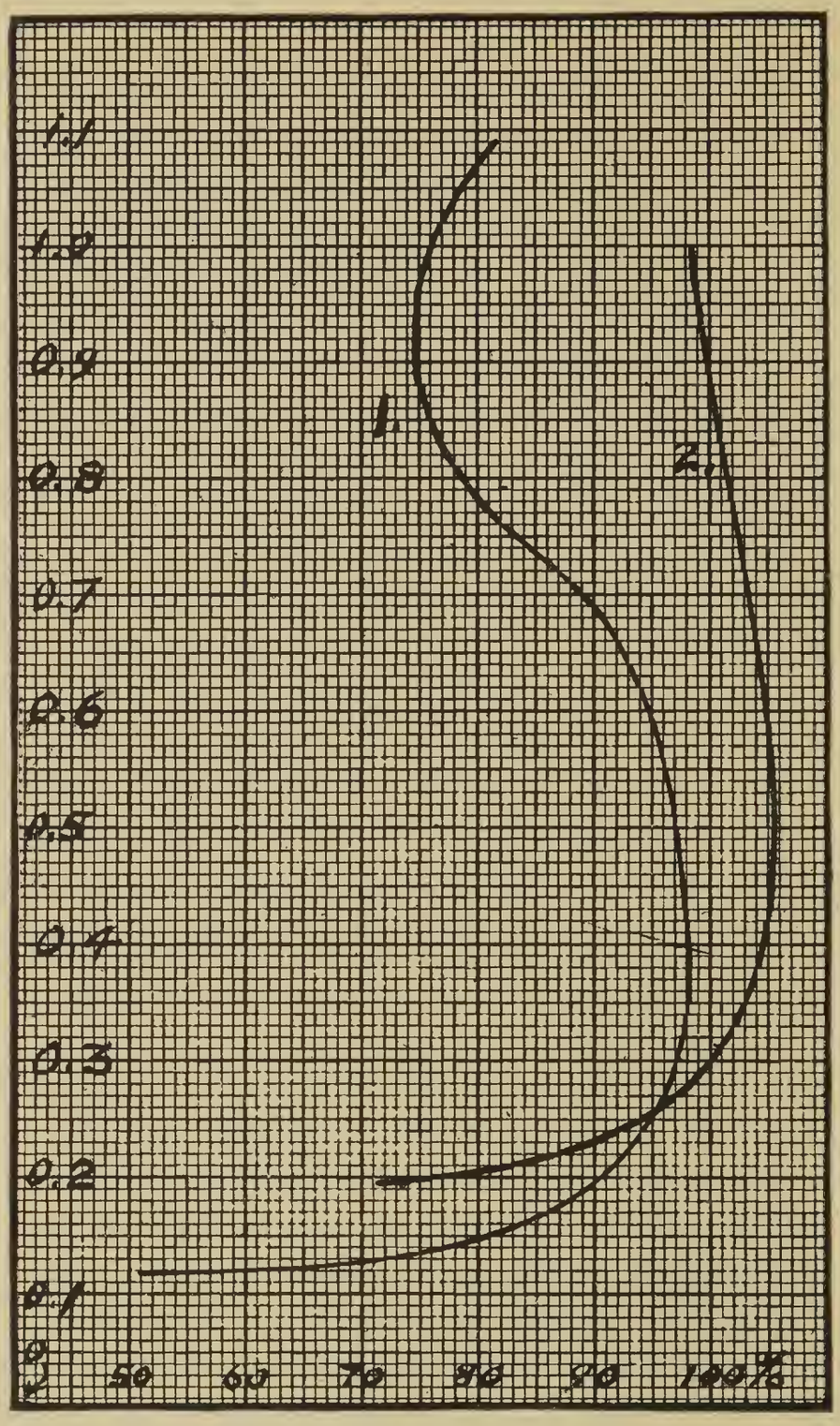


FIG. 2.

Showing the relation between the curves obtained from pure and impure electrolytes. Abscissæ, cathode efficiency in percent. Ordinates, concentration of Pb.
No. 1 Curve obtained from impure electrolyte.
No. 2 Curve obtained from pure electrolyte.

lead in the brine is unaffected by cyclic runs except by lowering the chlorine content.

The cathode efficiency is slightly higher in new brine than it is after impurities have built up in the brine solution. The differ-

ence between the cathode efficiency in an old and a new brine is shown in the set of curves in Fig. 2. The cause for the dropping off in efficiency was not definitely determined, although the presence of iron is probably the chief reason, being oxidized from ferrous to ferric iron at the anode, and reduced to ferrous at the cathode. A search for other causes yielded no results.

GENERAL RESULTS.

The saturated brine, after agitation with ore, contained from 1.0 percent to 1.4 percent of lead. With proper amounts of ore and brine, and enough acid to convert the lead carbonate or oxide to sulphate, the pregnant brine at room temperature will average 1.25 percent lead. Under these conditions nearly all of the lead, that is, lead in an oxidized form, will be extracted. A typical example is as follows: Starting with an ore containing 8.86 percent lead, one leach extracted 71 percent of the lead. By giving these tailings another leach with barren brine, a 95 percent extraction was obtained. Counter current leaching always gave about a 95 percent extraction of the lead.

The current densities it was possible to use were surprisingly large, considering the very low concentration of lead in the electrolyte. That these current densities were not excessive is shown by the fact that with a current density of 80 amperes per square foot (860 amp. per sq. m.) and a lead concentration of 0.4 to 0.6 percent, a cathode efficiency of 80 percent was possible; with a current density of 60 amperes per sq. ft. (645 amp. per sq. m.) and a lead concentration of 1 percent, a cathode efficiency of approximately 100 percent was obtained. The set of curves in Fig. 3 shows the relation between lead concentration and cathode efficiency for four different current densities. When the current density goes much above 60 amperes per square foot a great deal of hydrogen is evolved from the cathode. Hydrogen is also evolved at lower current densities when the lead tenor of the electrolyte becomes very low.

By referring to the set of curves in Fig. 3, we find that the best current density at which to start an electrolysis is 60 amperes per square foot. This should be maintained until the lead tenor falls to about 0.7 percent and then it should be dropped to 40

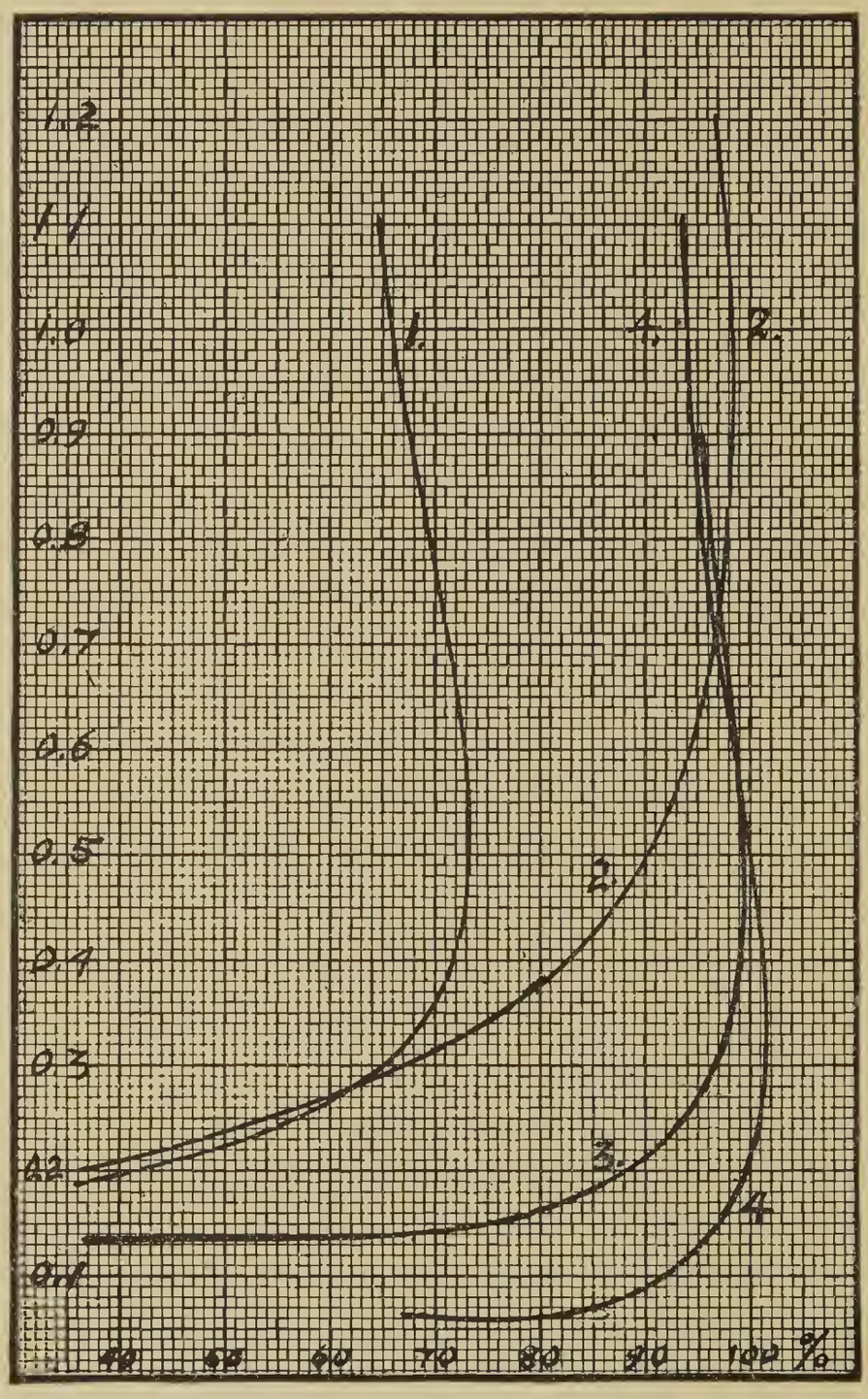


FIG. 3.

Showing the relation between cathode efficiency and concentration of lead in the electrolyte at different current densities.

Abscissæ, efficiency in percent. Ordinates, concentration of Pb.

Curve No. 1. At a current density of 80 amperes per sq. ft.
Curve No. 2. At a current density of 60 amperes per sq. ft.
Curve No. 3. At a current density of 40 amperes per sq. ft.
Curve No. 4. At a current density of 20 amperes per sq. ft.

amperes per sq. ft. (430 amp. per sq. m.). When 0.3 percent of lead is reached the current density should be dropped to 20 amperes per sq. ft. (215 amp. per sq. m.), and electrolysis stopped when the lead content falls to 0.1 percent. The cathode efficiency

will vary in two different runs having conditions as nearly alike as possible. One unexplained phenomenon is that the cathode efficiency was always lower at the beginning of an electrolysis than it was a little later in the run. This was also true if the electrolysis was stopped in the middle of a run and started again after an interval of time. It was thought at first that the ferric iron being reduced to ferrous iron at the beginning of the run was the cause of the low efficiency at the start, but it was found that the same thing occurred when no iron was present in the electrolyte. The cathode efficiencies on the whole are encouragingly high. In fact, during the greater part of most of the runs in which 40 amperes per sq. ft. or less were used the cathode efficiency was somewhat over 100 percent, averaging about 104 percent. These results may have been due to errors, but the work was carefully done, time measurements and current measurements being proved accurate and check samples being taken for analysis in each case. These results, therefore, compare very favorably with those obtained by Norman M. Bell, who found mono-valent lead dissolving from a lead anode during an electrolysis. (See Trans. Faraday Soc., **11**, 79-90, 1915.)

The voltage was very low, the average voltage for different current densities being as follows:

Current Density		
amp./sq. ft.	amp./sq. m.	Voltage
80	860	1.2
60	645	1.0
40	430	0.7
20	215	0.5

The cause of the low voltage is evident. The solution tension for iron is 0.42 volt and that of lead 0.12 volt as compared with zero for hydrogen. Therefore, the anodic solution of iron gives more energy than is necessary to precipitate lead cathodically. In fact, there is an initial voltage of 0.1 volt across the electrolytic cell before the external voltage is impressed. As no gas is formed there is no overvoltage of hydrogen or oxygen. Therefore, the impressed voltage is needed only to overcome the resistance of the electrolyte.

Owing to the high cathode efficiency, low voltage, and high electrochemical equivalent of lead, the power consumption per

lb. of lead is very low. With a current density of 20 amperes per sq. ft., which means a voltage of 0.5 volt and a cathode efficiency of 100 percent, as much as 17 pounds (7.7 kg.) of lead per K. W. H. may be deposited. This weight of deposited material is not even approached in the electrolysis of any other metal.

In one set of tests five electrodes were connected in series the same as in the copper series refining process, that is, the intermediate electrodes served as both anode and cathode on opposite sides. The comparison of series with multiple connections is as follows:

At a current density of 60 amperes per sq. ft.

	Series	Multiple
Cathode efficiency	62.2%	95%
Lead per K. W. H.	4.59 lb. (2.1 kg.)	6.83 lb. (3.1 kg.)

At a current density of 40 amperes per sq. ft.

	Series	Multiple
Cathode efficiency	68.9%	95%
Lead per K. W. H.	7.83 lb. (3.6 kg.)	8.65 lb. (3.9 kg.)

At a current density of 20 amperes per sq. ft.

	Series	Multiple
Cathode efficiency	63.2%	100%
Lead per K. W. H.	12.7 lb. (5.8 kg.)	16.1 lb. (7.3 kg.)

In the series connections of the electrodes neither the cathode efficiency nor the power efficiency is as high as in the multiple connections. The advantage obtained by the series connections, from a commercial standpoint, is: (1) a saving of the space taken up by the cathodes and a saving of the cost of the cathodes, and (2) smaller bus-bars because of the higher voltage and lower current required. On the other hand, the cathodes and bus-bars are permanent, and it would be only the first cost of installation that would be higher in the case of the multiple connections, while running costs would be lower because (1) more lead would be obtained per K. W. H. and (2) the cathode efficiency being higher the ratio between the amount of iron consumed and the lead deposited would be greater.

The trials with the insoluble carbon anodes gave very poor results. In the first place the voltage was high. There are two causes for the increase in voltage over that obtained with the iron anodes. First there is no energy obtained by anodic solution, and second there is the high overvoltage of the chlorine on the carbon anode. The voltages were as follows:

Current Density amp./sq. ft.	Voltage
80	2.6
60	2.3
40	2.1

The cathode efficiency near the beginning of the run was around 70 percent but fell rapidly. The brine absorbed large quantities of chlorine and became colored a dark greenish-yellow. This dissolved chlorine attacked the deposited lead sponge chemically and dissolved it nearly as fast as it was being deposited.

The deposit of lead sponge is much more compact and more easily recovered when deposited at a lower current density. When a very high current density is employed the lead sponge is fluffy and being filled with bubbles of hydrogen it floats on the surface of the electrolyte. It was also noticed that when the electrolyte was slightly acid rather than neutral that the lead sponge assumed a loose crystalline structure, in which form it could be more easily washed, could be dried more quickly with less oxidation, and could be melted down more readily.

Silver follows the lead in electrolysis. When treating an argentiferous ore from the Horn Silver Mine, of Frisco, Utah, some of the lead sponge assayed over 100 ounces of silver per ton. This silver could be recovered from the lead by Parke's process, or could be recovered from the solution before electrolysis by precipitation on sponge lead or on iron. A sample of lead obtained from some calcined tailings, after being melted and cast into an ingot was sent to the U. S. S. R. & M. Co. smelter at Midvale. The chemist there analyzed it and reported negligible impurities. It seems therefore that silver is the only substance of any importance that remains with the lead through the melting down treatment. Because of the very pure lead obtained it would probably be best to remove the silver before electrolysis and so avoid desilverizing the lead bullion.

ESTIMATED COSTS.

The accompanying sketch of a commercial-size electrolytic cell shows how one might be built for the electrolysis of the brine solutions of lead. On a cell of this design, the electrodes may be connected either in series or multiple. The drawing shows the arrangement for multiple connections. The arrangement for connecting in series would be the same except that the cathodes would be absent, and instead of having bus-bars down the sides, only the end plates would be connected with the external circuit. The pregnant solution would flow into one end from a feed launder and overflow at the other into a discharge launder. Agitation would be by air from holes in the six pipes running along under the electrodes. The sponge falling off of the plates would collect

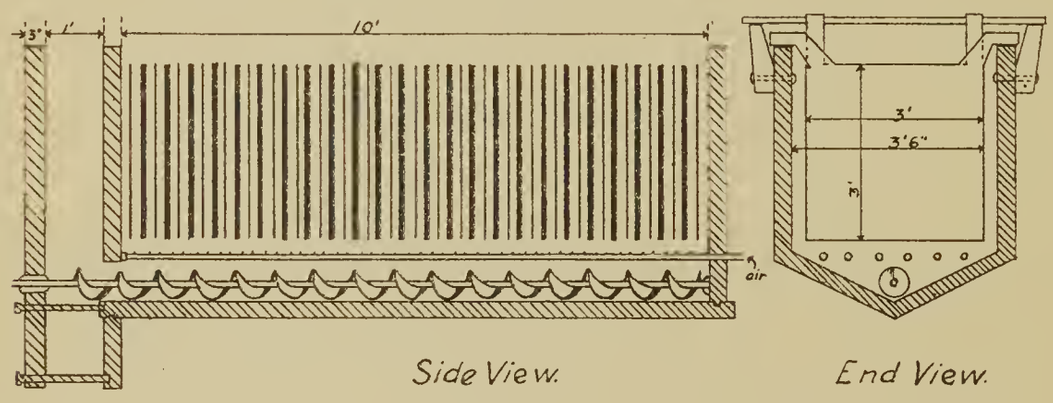


FIG. 4. Commercial-size Electrolytic Cell.

in the center of the V bottom and be carried to one end by the screw conveyor and then be discharged through the hopper arrangement along with a small amount of barren solution.

Because of the very high current densities used the multiple connections are out of the question, owing to the immense size of bus-bars that would be necessary. Therefore, estimates and calculations will be made on a process using a cell in which the electrodes are connected in series.

Following is an estimated cost of the erection of an electrolytic plant, exclusive of the leaching plant, to produce 10 tons of pure lead per day. It will be noticed that a margin of from 10 to 20 percent excess is allowed on all estimates above calculated figures.

In an electrolytic cell such as is shown, using series connections, 41 electrodes may be used. The electrodes being three feet square

there will be $3 \times 3 \times 40 = 360$ square feet (33.5 sq. m.) of cathode surface. Using a current density of 40 amperes per sq. ft. (430 amp. per sq. m.), which is conservative, and from data obtained assuming a cathode efficiency of 70 percent, we have:

$$\frac{360 \times 40 \times .70 \times 103.5}{96500 \times 1000} = 38.6 \text{ kg. per tank per hour.}$$

38.6 kg. = 85 lb. per tank per hour.
$85 \times 24 = 2040$ lb. or 1 ton per tank per day.

Therefore, ten tanks would produce ten tons lead per day.

The drop between electrodes will be about 0.7 volt.

$0.7 \times 40 = 28$ volts. 40 volts will be allowed for each tank.

$40 \times 10 = 400$ volts for ten tanks.

Therefore, figures will be made for a 450-volt generator to deliver 400 amperes, 360 amperes being needed.

$$\frac{400 \times 450}{1000} = 180 \text{ K. W.}$$

A 200 K. W. motor-generator set will therefore be needed. The excess power would be used in compressing air, operating pumps, etc.

By empirical measurement it was found that about 0.5 cu. ft. of air per minute is necessary for a three-foot length of electrode in order to give sufficient stirring of the electrolyte. Therefore, $40 \times 0.5 \times 10 = 200$ cubic feet of air would be required per minute for all of the tanks. 300 cu. ft. will be supplied.

Knowing the size and amount of equipment the estimated cost would be as follows:

One 200-K. W. motor-generator set, 450-volt, 400-ampere	$ 3,500.00
One 200-K. W. transformer, 45,000 to 560 volts	2,100.00
Ten wooden tanks at $100 per board foot, including construction, $50 apiece	500.00
Copper bus-bars, 0.5 inch in diameter, 100 ft., 64 lb. per 100 ft., at $.30 per lb.	30.00
Piping, 800 ft. at $.165 per ft.	130.00
Launders	100.00
Positive pressure blower, 300 cu. ft., at 3 lb.	420.00
Motor for blower, 25 H. P.	350.00
Small reverberatory for melting down 10 tons lead per day	500.00
Power plant building, $8 per sq. ft.	3,000.00
Electrolytic plant building, $2 per sq. ft.	4,000.00
Miscellaneous equipment	2,000.00
Total cost, erected	$16,630.00

Costs of the leaching plant are not included in the above total but have been variously estimated from $10,000 to $15,000, including crushing equipment and housing. In case a sulphide ore is being treated, the cost of roasters will also have to be considered.

OPERATING COSTS.

For operating costs, the following figures are approximate. They are made on the assumption that the material used is a mill tailing containing 10 percent lead in an oxidized form. The iron anodes are assumed to consist of cast iron, one inch in thickness.

Leaching 100 tons at $.80 per ton (for Horn Silver Mine ore)	$ 80.00[4]
Iron (estimating that 1 lb. iron is used for every 3 lb. lead deposited, and that it costs $40.00 per ton in anode plates), 3.3 tons	132.00
Power, 200 K. W. at 0.8c. per K. W. H	38.00
Labor, one foreman and four helpers on each of three shifts	57.00
Coal, 1 ton per day	3.00
Insurance and interest	20.00
Total for ten tons lead in one day	$330.00
Cost of producing one ton lead	$33.00
Value of one ton lead at 2¾c. lb	55.00[5]
Estimated margin of profit	$22.00

CONCLUSIONS.

The investigation on the electrolysis of lead in brine solutions is by no means complete. In the experimental work there is still a great deal to be learned about the causes of low cathode efficiencies; how the iron is thrown out of solution, conditions for obtaining the maximum concentration of lead with the smallest acid consumption, etc. The working details of a commercial plant have not been thoroughly worked out.

It would seem at first that it would not be possible to profitably electrolyze a metal of as low a value as lead. But when one considers the cheapness of the leaching agent and the high electrochemical equivalent of lead, together with the wonderfully high efficiencies possible, the problem assumes a different aspect.

[4] The leaching cost is calculated from the known acid requirements of a certain ore which contains a large amount of lead sulphate and only a small amount of lead carbonate. For most ores more acid would be required and hence the leaching cost would be higher.

[5] It will be noticed that the value of the lead is calculated on a 2¾c. per lb. basis. This is for the reason that in Utah, where this process has been developed, the cost of transportation to lead markets and refining is 1¼c. per lb. Hence our estimate really assumes a 4c. market. As a very pure lead can be obtained it is probable that only transportation costs need be considered, thus materially increasing possible profits.

If the process should be applied to mill tailings or a mine dump it looks as if a fair profit might be made. However, considering the low value of the product obtained, a 10 percent material could not be worked if a mining charge of several dollars a ton were added to the cost, although a lead carbonate deposit near the surface could stand considerable of a mining charge if a 15 to 20 percent ore were obtained.

Although electrolytic precipitation of the lead from brine leaching solutions is the principal subject discussed in this paper, the Department of Metallurgical Research of the University of Utah, in co-operation with the U. S. Bureau of Mines, has likewise been testing other methods of precipitation, and modified methods of leaching. We believe that such a method of treating lead ores will be found applicable to those ores at points distant from lead smelters, which are too low grade to ship, and which for any reason refuse to yield, as before stated, to gravity concentration. Many lead carbonate ores are of this type.

A paper presented at the Thirtieth General Meeting of the American Electrochemical Society, held in New York City, September 29, 1916, Mr. L. E. Saunders in the Chair.

CHARACTERISTICS OF SMALL DRY CELLS.

By C. F. Burgess.

The production of dry cells is a branch of the electrochemical industry which is exhibiting a remarkable growth. It thrives in spite of the oft-repeated predictions that the dry battery must give way to more efficient sources of electrical energy, that the central energy system is driving it out of the telephone field, that the small transformer is taking the place of batteries for bell and signal work, and that the magneto is replacing it for gas engine ignition.

The predicitons are not being fulfilled and the new use which has stimulated in a remarkable degree dry battery manufacture is the portable pocket light, known more commonly as the flash light.

The flash light is no longer a novelty or a device of restricted usefulness but it is a commodity of general utility, and those engaged in the manufacture believe the industry is only in its infancy. If fifty million represents the annual output of standard, or so called No. 6 dry cells, in this country, this figure may be multiplied several times to represent the number of small dry cells used for flash light and miscellaneous other purposes.

The flash light industry has been greatly stimulated by the development of the high efficiency miniature tungsten lamps, and of an influence equal in importance is the decided improvement in the qualities of the battery.

In spite of the financial importance and the wide-spread utility of small dry cells, little has been published on efficiencies, outputs, and other characteristics. This paper is presented as an approximate record of the performance of flash light cells, such as have been found on the market during the past year. It embodies the summary on tests of about 4,000 cells.

As an adjunct to manufacturing operations we have maintained

an experimental and testing department. In this department about 3,000 lots of experimental batteries, or over 30,000 cells have been made and tested during the past few years to determine the influence of impurities, of modification of construction and new ideas relative to improvement. In addition to experimental cells, periodical tests are made on our standard manufactured product, in comparison with the product of other manufacturers on the market.

There are no generally accepted methods of testing by which the characteristic of small cells can be expressed with mathematical accuracy and we have been forced to devise our own methods, following as far as practicable those recommended by the Dry Battery Testing Committee reported in the Transactions of the American Electrochemical Society, Vol. XXI, 1912.

The two most important characteristics by which the value of flash light batteries may be determined are ability to furnish light over a period of time, or its capacity, and its ability to withstand deterioration when not in use, or its shelf life. Other characteristics of importance are voltage, recuperation, uniformity, size, cost.

Since by far the most important use of small cells is for flash light service, the tests aim to parallel as far as practicable this type of service.

The flash light lamps, or bulbs, as standardized by the large manufacturers, are rated as in Table I.

TABLE I.

Flash light bulbs	Volts	Amperes	Type of Battery to be Used	Ohms Resistance per cell
Clear	2.7	0.35	2 cell—tubular type	3.84
	3.8	0.35	3 cell—tubular type	3.62
	2.9	0.35	2 cell—tubular type	4.14
	4.0	0.35	3 cell—tubular type	3.81
Opal back	2.5	0.35	2 cell—case type	3.57
	3.8	0.35	3 cell—case type	3.62
	2.5	0.25	2 cell—case type	5.00
			Average	3.94

The most obvious method for a user to determine how many hours or minutes of lighting service he can secure from a battery is to put the battery in the case and note the length of time that the lamp will give a usable light. This method is not of much service to the small user as it is laborious, and consumes his battery. It is of even less use to the manufacturer for accurate comparative purposes because no two users will agree upon the same degree of brilliance at which the lamp filament ceases to give a usable light. In other words, there is no definite "end point." Furthermore, incandescent lamps are not accurately standardized and vary decidedly in their initial resistance and in their resistance after a time of burning.

The standard method of capacity test which has been used by our laboratories and by several other manufacturers is to adopt a fixed standard resistance through which the individual cell is discharged, and noting the length of time on discharge required for the cell to drop to a certain voltage.

From the above table it is seen that four ohms is close to the average resistance of the common sizes of standard lamps, and this is adopted as the standard. This is the resistance recommended by the Committee on Standard Methods of Testing Dry Cells, Transactions of the American Electrochemical Society, Vol. XXI, 1912.

As to the end point, a voltage of 0.5 across the cell terminals when delivering current to the 4 ohms resistance is taken as indicating when the current has fallen so low as to give a non-useful light. There is room for argument as to what voltage should be taken as the end point, the answer hinging on the question, how dim may the light be before burning useless? With the pressure at one-half volt per cell the light is dull, enough to read a clock dial, but not enough for general flash light service. When it is considered, however, that a battery after it has dropped to 0.5 volt per cell on continuous discharge has the capacity of recuperating to some extent when left on open circuit, and can then give a more brilliant light for a short period, it becomes fair to take the 0.5 volt as the standard end point.

Capacity or Time of Burning. Our standard method of capacity test then consists in connecting an individual cell to a resistance coil of 4 ohms, and discharging continuously until this

voltage drops to 0.5 volt. The readings which are taken are the initial open circuit pressure, the short circuit flash through an ammeter, the voltage at the instant of connecting to the 4-ohm coil, and readings of voltage every hour, or half hour during the discharge. Our testing period is eight hours per day. Most of the flash light cells will drop to 0.5 volt during the eight-hour period, though the larger cells will run beyond this, therefore giving some chance to recuperate before the beginning of the following test period.

In connecting the cells to the resistance terminals it is important to avoil contact resistances. This can be done practically by having the resistance coil terminals soldered to Fahnestock clips. The cells are prepared for test by soldering tinned copper wire leads to the zinc and the brass cap of the cells. When a battery of two or three cells is to be tested its terminals are connected to two and three of the 4-ohm coils connected in series.

Durability of Shelf Test. Of importance equal to the capacity test is the test showing the ability of the battery to stand idle without losing its capability of service. This is usually designated the "shelf-life test."

If we may judge from labels on batteries, and the wording of the guarantees of the makers, it appears to be a general practice of manufacturers to judge deterioration by the falling off in open-circuit voltage. Thus we read "This battery is guaranteed not to depreciate in voltage more than ten percent in ten months, provided battery has not been in use." Such a guarantee is of little real interest to the user because a battery may deteriorate fifty percent or more in ability to deliver current while still maintaining closely its original open-circuit voltage.

We have found from long experience and a great many tests that a far better method of determining the deterioration going on within the cell is by measuring the short circuit flash which the cell gives when connected momentarily to the ammeter. Thus a cell which gives an initial flash of eight amperes when new may drop to four amperes after six months, and this indicates roughly a depreciation in capacity of fifty percent. While the decrease in flash is not strictly proportional to the decrease in ampere-hour capacity, it is nevertheless a far better indication

than is the dropping in open-circuit voltage. For want of a better test therefore we have adopted this as our standard.

The method of procedure is to place the cell on the shelf after taking an initial reading of voltage and short circuit current. At the end of each month period the tests are reported and results recorded. For the larger sizes of flash light cells the test period covers a year, and for the smallest sizes from six to eight months. At the end of such periods the cells are taken from the test shelves, usually in a run-down condition, and numerical rating is given by determining the percentage decrease in flash during such period and dividing by the number of months to give the average monthly percentage of deterioration.

Voltage. Dry cells vary in initial voltage far less than they do in other characteristics. They are similar in that they all use zinc and carbon electrodes, an electrolyte of sal ammoniac, and zinc chloride, and a depolarizing mass of manganese dioxide and conducting carbon. The grades of materials employed, as well as the methods of manufacture, influence to a small degree the voltage. Thus, cells on the market will be found to have a voltage of from 1.45 to 1.55 or even 1.6.

Recuperation. The ability of a battery to "recuperate" or to come back to its ability to give a good light after resting for a period is an important quality in the opinion of some authorities and of less importance in the opinion of others. This property can be given to a cell by certain variations in methods of manufacture. Thus a coarser grade of manganese will show a higher recuperative ability than will a very fine-powdered, more active grade. In general, it may be considered that high recuperative ability is inconsistent with ability to deliver current constantly without serious dropping in voltage.

Uniformity. If a manufacturer could discover some method of construction so that each cell would be exactly like the best which he can produce, it would be a great achievement in the improvement of quality. Some of the reasons for variation are known and others are mysterious. There is no doubt that care in selection and purification of material, and more especially care in assembling them, are important factors. A product which has a comparatively high rate of deterioration will show greater

non-uniformity in the hands of the users than will a product which has a low rate, this being due to the variation in the period from manufacture to use.

Size of Cells. Small cells are found on the market in a great variety of sizes and forms of battery. The most common form is the two-cell and three-cell tubulars for use in metal or fibre cases. Of almost equal importance is the two-cell or three-cell battery of smaller dimensions, the cells being placed side by side for use in flat cases and commonly designated as the "case" type.

The most commonly used dimensions of cell construction are given in Table II.

TABLE II.

Shop No.	Dimensions of Cells	Type of Battery
2	2.25 in. long x 1.25 in. diameter (57.2 x 38.8 mm.)	For tubular batteries
1	1.8125 in. long x 0.9375 in. diameter (46.1 x 23.8 mm.)	For tubular batteries
5	2.125 in. long x 0.75 in. diameter (54 x 19.1 mm.)	For case batteries
4	1.875 in. long x 0.625 in. diameter (47.7 x 15.9 mm.)	For case batteries
7	1.5625 in. long x 0.5625 in. diameter (39.7 x 14.3 mm.)	For case batteries
7R	1.875 in. long x 0.5625 in. diameter (47.7 x 14.3 mm.)	For tubular batteries

From our laboratory test records a compilation has been made from tests on about four thousand cells made during the period from Feb. 1, 1915, to April 1, 1916, and showing the relative performance and characteristics of cells of various brands found on the American market.

It has of course been impossible to place all cells on an equal basis as regards freshness of manufacture, but the attempt has been made to prevent inequality as far as possible by getting fresh stock through jobbers and dealers who get frequent shipments from the manufacturers.

In presenting the results there are obvious reasons why the trade names may not be used and the various brands are indicated by the letters *A* to *J* respectively.

TABLE III.

Capacity or hours of Burning.

Brand	Size of Cells—Inches					
	2¼ x 1¼	1 13/16 x 15/16	2⅛ x ¾	1⅞ x ⅝	1 9/16 x 9/16	1⅞ x 9/16
A	13.25	3.5	3.75	1.9	56 min.	70 min.
B	....	3.6	4.2	1.7	....	....
C	10.5	2.	...	.85	13 min.	....
D	13.25	5.	4.2	2.0	63 min.	66 min.
E	13.75	4.1	...	1.4	40 min.	....
F	9.25	3.1	2.5	1.25	34 min.	45 min.
G	8.75	3.2	2.	1.1	....	....
H	13.25	4.3	4	1.9	40 min.	75 min.
I	9.00	..	...	1	....	....
J	...	..	...	1.1	....	....

TABLE IV.

Durability or Shelf Wear.

Expressed in Monthly Percentage Reduction in Flash.

Brand	Size of Cells—Inches					
	2¼ x 1¼	1 13/16 x 15/16	2⅛ x ¾	1⅞ x ⅝	1 9/16 x ⅝	1⅞ x 9/16
A	3.66%	8.3	9.2	9.	12.	9.3
B	1.55	6.45	9.1	10.	..	..
C	1.87	3.83	..	5.	25	..
D	2.40	5.7	5.0	8.1	6.6	10.5
E	5.10	7.5	..	9.6	14.	15.3
F	14.3	11.2	14.1	25.0	..	14.0
G	10.8	12.	10.	22.0	25	..
H	10	12.5	9.1	15.0	27	13.3
I	2.64	...	...	6.2	..	..
J	...	...	...	...	..	..

From the capacity tests it is to be noted that the best cells have a capacity about 100 percent above the poorest, and from the durability tests the differences are much greater. The brand showing the smallest deteriorations shows also the smallest capacity, and emphasizes the fact that the factors which contribute to long life are not those which develop large ampere-hour capacity. In practice it is necessary to choose standard

values of capacity and durability and combine them in a product to give greatest usefulness.

For guidance in our testing and manufacturing, a set of standard curves has been prepared showing what cell performance may be expected. These curves showing capacity requirements are given herewith.

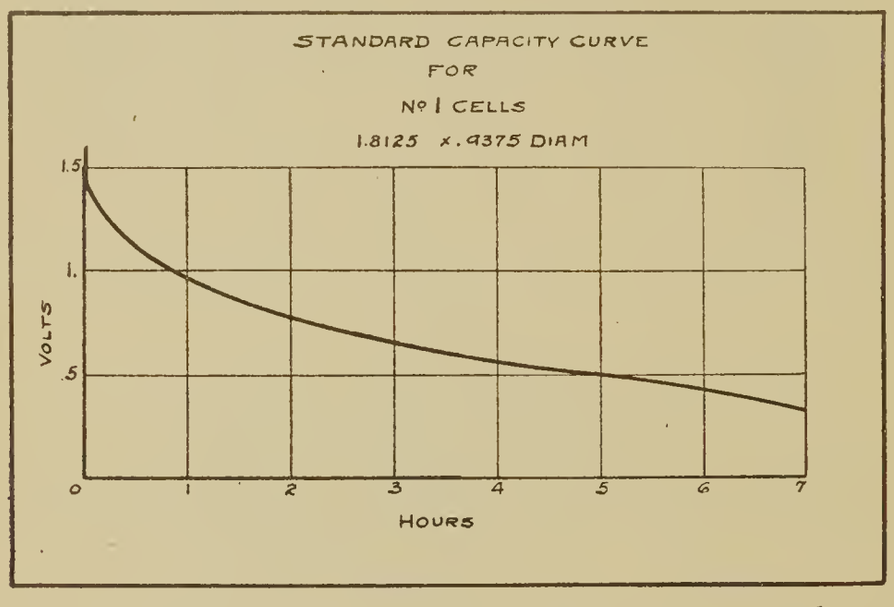


FIG. 1.

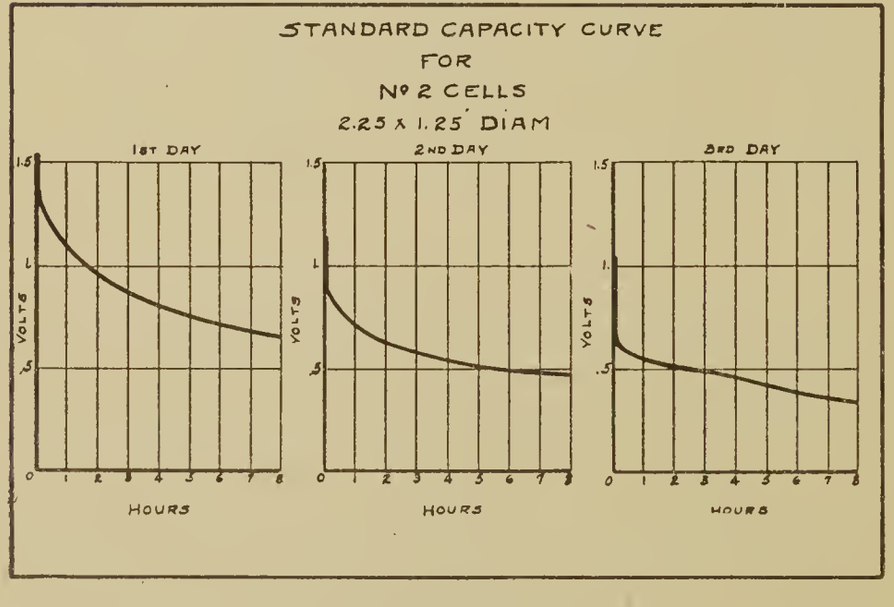


FIG. 2.

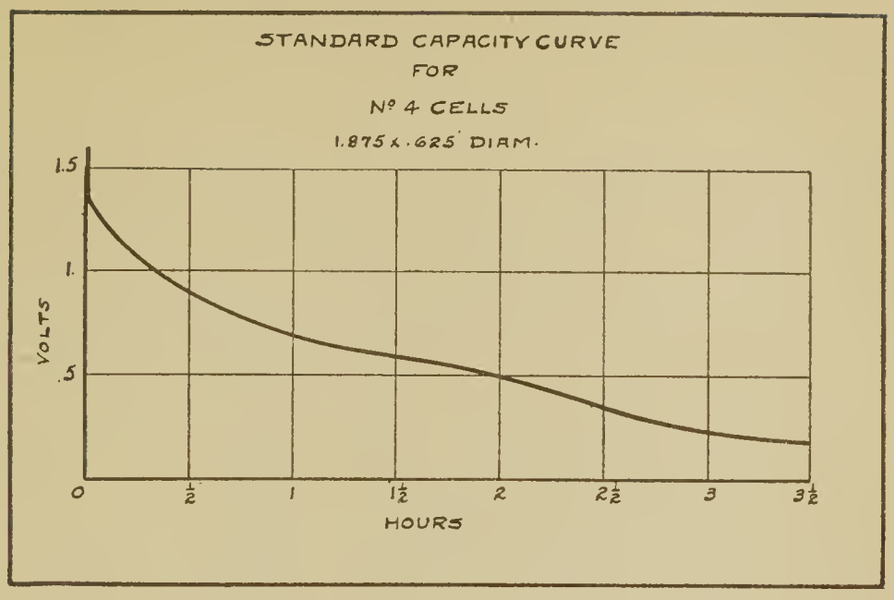


FIG. 3.

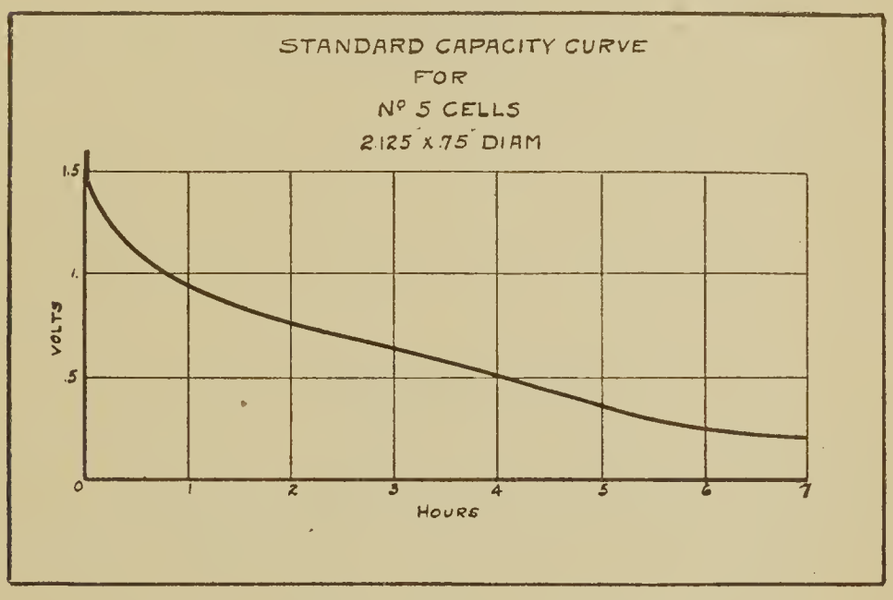


FIG. 4.

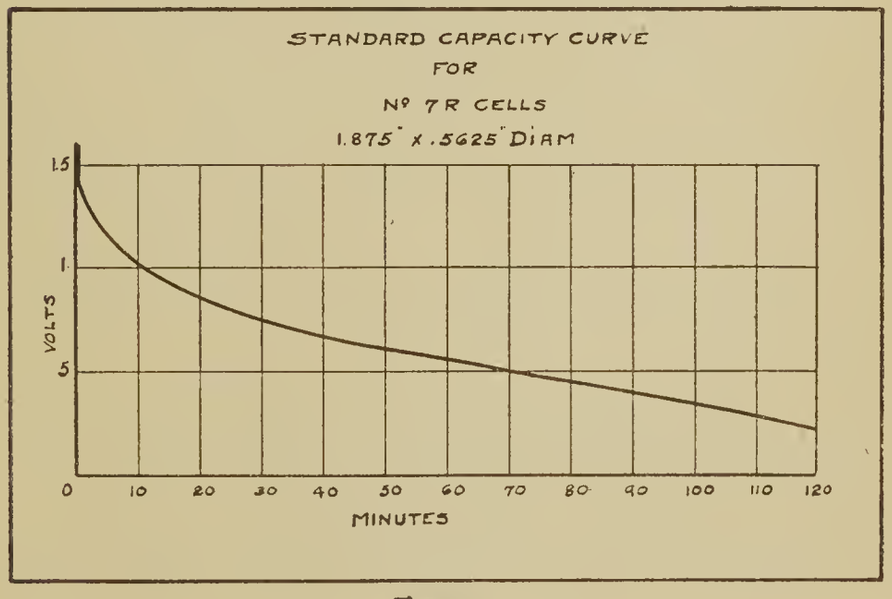


FIG. 5.

To summarize the desirable and attainable qualities is the purpose of Table V.

TABLE V.

Performance That Should be Expected from Good Quality of Cell.

Cell Dimension	Capacity Minutes	Percent Monthly Deterioration
2.25 x 1.25 in. (57.2 x 38.8 mm.).....	960	Under 4%
1.8125 x 0.9375 in. (46.1 x 23.8 mm.)...	300	" 6
2.125 x 0.75 in. (54 x 19.1 mm.).....	250	" 8
1.875 x 0.625 in. (47.7 x 15.9 mm.).....	120	" 10
1.5625 x 0.5625 in. (39.7 x 14.3 mm.)....	65	" 12
1.875 x 0.5625 in. (47.7 x 14.3 mm.)....	70	" 12

C. F. Burgess Laboratories,
Madison, Wis.

DISCUSSION.

A. T. BALDWIN: A perusal of tables Nos. 3 and 4 on page 263, taken along with the following quotation, brought up the question as to whether or not there was a discrepancy between them. To quote, "The brand showing the smallest deteriorations shows also the smallest capacity, and emphasizes the fact that the factors which contribute to long life are not those which develop large ampere-hour capacity." Considering this statement entirely from the point of view of the merchant selling flashlights, this means that the brand standing up best on his shelves is the least likely to satisfy his customers. A careful study of the tables referred to does not seem to me to bear out the author's contention so conclusively.

Out of six cases where comparison is possible, in just two instances do the cells with the smallest deterioration have also the smallest capacity for their respective groups. These are brand *C*, sizes 1 13/16 by 15/16 in. (46.1 x 23.8 mm.) and 1⅞ by ⅝ in. (47.4 x 15.9 mm.). Brand *C* 2¼ by 1¼ in. (57.2 x 38.8 mm.)

cells rank third from the greatest in capacity and lowest in deterioration among eight brands where the comparison can be made. In the 1 9/16 by 9/16 in. (39.7 x 14.3 mm.) groups, brand *C* stands lowest in capacity and next to highest in deterioration, in five cases where comparisons can be made. Passing to brand *D*, the data seem to indicate that great capacity and low deteriorations are not incompatible. For the 2⅛ by ¾ in. (54 x 19.1 mm.) and the 1 9/16 by 9/16 in. (39.7 x 14.3 mm.) groups, brand *D* cells have the greatest capacity and smallest deteriorations for their groups. In no group does this brand rank lower than third from highest in capacity nor higher than third from the lowest in deterioration. Brand *A*, sizes 1 9/16 by 9/16 in. (39.7 x 14.3 mm.) and 1⅞ by 9/16 in. (47.7 x 14.3 mm.) rank very high in capacity and very low in deterioration, while brand *H* shows a general tendency to have a very low capacity and high depreciation which seems to be the converse of the author's assertion and more in accord with my expectations.

To recapitulate, there are as many cases where a brand of cells having the smallest deteriorations have the greatest capacity for their groups, as there are cases where the brand of cells having the smallest deterioration have also the smallest capacity for their groups. Brand *C*, where the cells having low capacity and deterioration are found, is characterized by having low capacity for all sizes and a varying deterioration percentage, whereas brand *D* has a consistently high capacity and low deterioration rate, which is all the more remarkable when the lack of uniformity of all the other brands is considered. While I am unable to argue on the question whether service capacity can only be obtained at the expense of shelf life, or *vice versa*, it does seem that the greater weight of the data presented here does not show them as dependent on one another.

It would add to the value of the paper and the ease of checking the results recorded if the author had included the exact end point he used in terminating his shelf life tests.

C. A. Gillingham (*Communicated discussion, read by W. C. Moore*): We have read Mr. Burgess' paper with considerable interest and would like to add a few remarks on the value of the capacity test as therein described.

While this test is well fitted for a control test on some one brand, for following its uniformity of quality, we feel it is not so well adapted to the quantitative comparison of different brands, which, being made under different specifications, will have very different characteristics.

In the first place, the discharge through 4 ohms does not give the same actual life as does a discharge through a standard miniature lamp of 0.35 ampere drain. The resistance of these lamps at the rated voltage approximates 4 ohms per cell, as shown by Mr. Burgess in his Table I, but as the voltage across the lamp is reduced the resistance decreases to a very marked degree as shown by the following figures which are representative:

Volts per cell across lamp	Resistance of lamp in ohms per cell
1.5	4.06
1.27 (rated voltage)	3.72
1.0	3.32
0.5	2.40

As the voltage of the cell on capacity test during the greatest part of the test is well below 1.0 volt, it is evident that 4 ohms is too high a resistance to use as representative of lamp service. We find 2.75 ohms about correct, giving the same life as an actual discharge through a 0.35 ampere lamp.

It will be found that a 4-ohm test may show a different relation between two brands of cell than does a 2.75-ohm test. As the latter is closer to actual lamp service, the 2.75-ohm figure is the more reliable for comparative purposes.

	Capacity through 4 ohms	Capacity through 2.75 ohms
Cells 2¼ x ¼ Brand *A*	894 min.	514 min.
Brand *B*	589 "	381 "
Ratio *A*:*B*	1.52	1.35

Carrying out a capacity test in 8-hour periods seems to us liable to lead to unfair conclusions. Consider the case of two cells which, if run continuously, would give 7½ and 8½ hours respectively. Now in the case of the 8½-hour cell the interruption of the test after 8 hours will allow it sufficient recuperation to give an additional 3 hours service the following day, bringing its total to 11 hours. The 7½-hour cell is not allowed this advantage and, therefore, suffers an unfair comparison.

The "end point" to be used in determining the life of the cell is an important item, as the shape of the curve varies considerably in different brands of cell. One cell may hold well at the beginning and drop off more rapidly toward the close of the test, while another may drop off rapidly at the beginning and hang on for the rest of the test just above the end-point voltage. The first cell will unquestionably give a much better light during its life than will the second, and this point is as important as the actual length of service. By using the results to a higher end point, say 0.75 volt, as well as those to the 0.50 volt cut-off, we get an idea of the quality as well as the length of the service. The following figures will show the lack of relation between the results to these two end points.

Brand	Capacity test run to 0.75 volt	Capacity test run to 0.50 volt
A	306 minutes	950 minutes
B	452 "	894 "
Ratio *A*:*B*	0.68	1.06

We believe, therefore, the 0.50 volt results should not be considered alone, but in relation to the general shape of the discharge curve.

While these points I have mentioned may serve to make possible a more accurate rapid comparison of capacity, yet it is quite impossible by any continuous or nearly continuous test of short duration to gain an estimate of the relative value to the actual user of two different brands of cells. No consumer uses his flash-light continuously. The great majority of flash-light batteries are burned less than five minutes a day or give service over a period of months or at least weeks. A test much more closely representing this actual service consists of discharging the cell five minutes daily. A resistance of 4 ohms and an end point of 0.5 volt are employed. In this intermittent test the shape of the curve is very different from the continuous curve, holding up almost horizontal till nearly the end, where it falls off quite rapidly. This brings the 0.75 and 0.50 volt end points quite close together, so that the matter of which to consider is of little importance. Also, in this type of test 4 ohms more nearly represents lamp service than would 2.75 ohms, because the curve is practically all in the higher voltages where the lamp resistance approximates 4 ohms.

This test, covering as it does a period of several months in the case of the larger size flash-light cells, includes in itself the practical effects of capacity, recuperation and shelf life deterioration under service influence. It is certainly more representative of true value than any rapid continuous test, and its results may be entirely contrary to continuous test indications. We are giving below a table showing the discrepancies between the two methods of testing applied to a number of makes of 2.25 x 1.25 inch cells.

Brand of Cell	Continuous Capacity test. 2.75 ohms to 0.50 volt end point	Intermittent Capacity test 5 minutes daily. 4 ohms to 0.50 volt end point
A	542 minutes	450 minutes
B	463 "	81 "
C	381 "	660 "
D	515 "	577 "
E	509 "	473 "

For instance, brand *A*, which has the best continuous capacity, has to yield precedence to brands *C*, *D* and *E* when judged by the more indicative intermittent test. And brand *C* which stands highest by the intermittent is comparatively poor in continuous capacity. Similar instances may be found among smaller size cells.

It is, therefore, evident that actual capacity to serve is not so simply measured as would appear from Mr. Burgess' paper, and is not satisfactorily accomplished by any rapid continuous method. It is essential that a truly indicative test must approximate actual average service conditions, standardized for the sake of uniformity. Naturally such tests require time and patience and their operation is expensive, but both time and expense will be found essential if true comparisons are desired.

Carl Hering: This paper brings up the old question again, when is a battery discharged? This has been a much mooted question for many years. I might therefore call attention to a statement I made in a paper about twenty years ago, that if batteries are discharged at a constant wattage, a very sharp point is obtained at which the discharge ceases. We all know that the curves either of current or voltage fall in such a way that it is difficult to say where they stop, but if you discharge at constant wattage, that is, at constant power, the curve of discharge is absolutely horizontal and at the end it falls perpendicularly, and therefore gives a very sharp point at which the battery is dis-

charged. This method does not represent the real way in which the battery is used in practice, but it approximates it, because when a battery does not give the necessary power for which it is intended, it is considered discharged. It seems therefore to be a better method of comparison of different batteries than any other. Toward the end of the curve you must increase the current very rapidly to keep up the wattage, and the test is therefore a little more tedious to make.

J. W. RICHARDS: Since the two factors are high capacity and long shelf life, would not the product of these two give a numerical index of the value of the battery?

C. F. BURGESS (*Communicated*): The writer of this paper finds in the discussion valuable additions to our published information on dry cells. He can agree with the assertion that there is no necessary and exact relationship between shelf life and capacity.

He has, however, pointed out the apparent relationship, based upon extensive experiences in constructing and testing experimental cells, during which it appeared that most of the departures from the established practices which would produce high capacity had a tendency to shorten shelf life. This relationship apparently does hold definitely as between the various brands of product now on the market.

Whether or not four ohms per cell is a satisfactory standard for testing practice is one of the matters which should be decided before standard practice can be adopted. There are good reasons for the use of a short-time continuous-discharge test and, as emphasized in the discussion, there are equally good reasons for using intermittent tests covering a long period. The choice depends largely upon expediency, and where a short test is followed its results should be used with the full knowledge of the limitations.

If this paper with the discussion indicates that those interested in dry-cell construction are willing to compare notes and testing methods, and to study the question of standard tests, it has fully achieved the object desired. It is hoped that a report may be prepared for submission at a later meeting embodying definite recommendations.

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EFFECT OF TEMPERATURE UPON THE PERFORMANCE OF THE EDISON STORAGE BATTERY.

By L. C. Turnock.

Since the storage battery generally finds service in climates where there is a comparatively great difference between the temperatures of the winter and summer seasons, its performance and variation of capacity with changes of temperature in such localities, or under analogous thermal conditions is of importance commercially. Conditions of service the battery is commonly called upon to meet are, first, a charge at one temperature with a subsequent discharge at a lower temperature; secondly, a charge at one temperature followed by a discharge at a higher temperature, and thirdly, both charge and discharge at either high or low temperatures.

It is common observation among users of storage batteries that the available capacity decreases with lowering of temperature. In vehicle service this is manifested by the fact that it is found impossible either to obtain the mileage per charge or to maintain the delivery schedules that experience had shown possible at higher temperatures. It is considered good practice not to discharge a battery, while it is delivering a certain recommended current, below a specified terminal voltage per cell. This so-called cut-off voltage is a purely arbitrary value, to which the capacity of the battery is measured. It is entirely permissible to carry the discharge further and without injury to the battery, but the selection of the value is prompted by the fact that the battery will give its best service and show its best practical efficiency if the discharge is not carried beyond this limit.

Batteries discharged at low temperatures (during cold seasons) appear to have less capacity because the voltage limit of discharge is reached sooner than if the battery were discharged at higher temperatures. The temperature coefficient of resistance of the

electrolyte being negative, the lower temperatures cause a higher internal resistance, which in turn results in a higher internal (IR) "drop" and consequent lower terminal voltage. Moreover, since the electrical energy of the battery is a result of certain chemical reactions and the speed of chemical reactions, in turn, is a direct function of temperature, it follows that the amount of available active material would be less, and perhaps an earlier realization of the cut-off voltage should be anticipated.

In order to obtain an analysis of the performance of the battery and to note how the different electrodes function upon charge and discharge, it is necessary to employ an auxiliary test-electrode. It is desirable that this should be practically insoluble in the electrolyte, have no deleterious effect upon the cell, and be non-polarizable when functioning either as anode or cathode toward the electrodes. The latter characteristic will insure constancy of its electrical potential, which is highly essential for comparative tests. Of a large number of substances experimented with to determine their applicability as auxiliary electrodes, the most satisfactory and practical seems to be a portion of one of the nickel hydrate tubes composing the positive plates of the battery. Properly insulated from the battery plates and container with perforated rubber sheeting, and previously charged, such an electrode will remain remarkably constant in potential and for practically an unlimited number of measurements, provided it is kept in the electrolyte to prevent drying out when not in use. Observations of difference of potential may be taken with a low scale voltmeter, which require small current values for operation, instead of a potentiometer without appreciably disturbing the constancy of its potential.

While the selection of the cut-off voltage per cell on discharge is purely arbitrary, the same is more or less true of the charging and discharging current rates for the battery. Several factors influence the designation of "normal" charge and discharge rates. The rate of dissipation of the heat due to internal electrical losses should become equal to the rate at which it is generated before a temperature is attained that will be detrimental to the life and efficiency of the battery or cause trouble in any other manner. Secondly, inasmuch as the rate of liberation of the electrolyte ions, which effects the oxidation and reduction of the active mate-

rials on charge and discharge, is proportional to the strength of the current passing, such a current density should be employed as will most efficiently cause the desired oxidation and reduction. It is possible to liberate the ions more rapidly than they can be absorbed chemically by the active materials; obviously, such a condition will result in a loss of efficiency, which it is desirable to avoid as far as practicable. From an economical standpoint such a rate should be employed where the advantage gained by a more rapid charge and discharge will just equalize the disadvantage incurred through loss in efficiency; in practice the former condition will always outweigh the latter.

In order to complete a cycle of charge and discharge within a convenient length of time a current rate of fifteen amperes was employed. Although this value is about twice that recommended as a "normal" rate, nevertheless, the results obtained therewith under variable temperature conditions should be entirely comparable to those obtained at a lower rate. The cells under test were placed in a bath electrically heated and thermostatically regulated. It was possible to control automatically all temperatures to within one-tenth of a degree. The cells were charged on all runs (except as noted) for a period of four hours, which is equivalent to an apparent input of sixty ampere-hours, and their available capacity noted to the time the terminal voltage reached 0.5 per cell. All electrical readings were made with precision instruments.

Although all batteries before being shipped from the factory receive a sufficient number of cycles of charge and discharge to bring them up to a point where they will deliver at least their rated capacity, nevertheless, they appear to increase slightly in capacity with more or less constant and continued use. Such an increase in capacity is no doubt due to an increased porosity and consequent greater penetrability of the active mass by the electrolyte ions with the result that a greater amount of it is thereby rendered accessible and hence available. In order to make the conditions under which the tests were run conform as far as possible with those of cells that have been in commercial use for some time upwards of thirty cycles of charge and discharge were administered to the cells before the test runs recorded were begun.

Table I.

Charging Rate—15 Amperes. Discharging Rate—15 Amperes.
Temperature—50° C. or 122° F.

	Cell A.		CHARGE	*Cell B.*		
Time	Cell Potential in Volts	Potential + Elect. to Test Electrode Volts	Potential — Elect. to Test Electrode Volts	Cell Potential in Volts	Potential + Elect. to Test Electrode Volts	Potential Electrode to Test Electrode Volts
9:05	1.833	0.013	1.82	1.795	0.02	1.775
9:15	1.913	0.053	1.86	1.90	0.074	1.826
9:30	1.925	0.052	1.86	1.88	0.078	1.812
9:45	1.912	0.065	1.847	1.87	0.070	1.80
10:08	1.910	0.080	1.83	1.872	0.082	1.79
10:25	1.915	0.135	1.78	1.888	0.138	1.75
10:45	1.922	0.102	1.82	1.888	0.110	1.778
11:05	1.928	0.108	1.82	1.893	0.113	1.78
11:25	1.938	0.118	1.82	1.905	0.125	1.78
11:45	1.948	0.118	1.83	1.915	0.128	1.787
12:05	1.960	0.125	1.835	1.925	0.135	1.79
12:25	1.980	0.130	1.850	1.94	0.135	1.805
12:45	2.000	0.134	1.866	1.96	0.140	1.82
1:05	2.005	0.130	1.875	1.968	0.136	1.832
			DISCHARGE			
1:10	1.12	—0.06	1.18	1.13	—0.065	1.195
1:20	1.04	—0.12	1.16	1.07	—0.012	1.190
1:30	1.00	—0.16	1.16	1.04	—0.150	1.190
1:40	0.978	—0.174	1.152	1.02	—0.160	1.180
1:50	0.968	—0.185	1.153	1.00	—0.186	1.186
2:10	0.927	—0.218	1.145	0.97	—0.210	1.180
2:30	0.90	—0.235	1.135	0.948	—0.227	1.175
2:50	0.865	—0.255	1.120	0.925	—0.245	1.170
3:10	0.808	—0.295	1.103	0.88	—0.278	1.158
3:30	0.733	—0.340	1.083	0.80	—0.330	1.130
3:50	0.680	—0.400	1.08	0.73	—0.390	1.120
4:10	0.588	—0.492	1.08	0.659	—0.451	1.110
4:15	0.500	—0.590	1.09	....	....	....
4:19	....	....	....	0.500	—0.630	1.130

Table II.

Charging Rate—15 Amperes. Discharging Rate—15 Amperes.
Temperature—60° C. or 140° F.

	Cell A.		CHARGE	*Cell B.*		
Time	Cell Potential in Volts	Potential + Elect. to Test Electrode Volts	Potential — Elect. to Test Electrode Volts	Cell Potential in Volts	Potential + Elect. to Test Electrode Volts	Potential — Elect. to Test Electrode Volts
9:05	1.828	0.048	1.780	1.79	0..055	1.735
9:15	1.85	0.060	1.790	1.81	0.080	1.730
9:25	1.885	0.075	1.81	1.85	0.075	1.775
9:35	1.915	0.090	1.825	1.875	0.095	1.780
9:45	1.912	0.10	1.812	1.86	0.10	1.760
9:55	1.90	0.10	1.80	1.85	0.10	1.750
10:05	1.895	0.10	1.795	1.84	0.095	1.745
10:25	1.90	0.105	1.795	1.855	0.110	1.745
10:45	1.90	0.11	1.79	1.86	0.115	1.745
11:05	1.90	0.115	1.785	1.86	0.120	1.74
11:25	1.90	0.11	1.79	1.867	0.127	1.74
11:45	1.908	0.12	1.788	1.872	0.132	1.74
12:05	1.912	0.122	1.79	1.872	0.127	1.745
12:25	1.915	0.125	1.79	1.88	0.130	1.75
12:45	1.92	0.130	1.79	1.885	0.135	1.75
1:05	1.932	0.132	1.80	1.895	0.140	1.755
			DISCHARGE			
1:10	1.09	—0.075	1.165	1.12	—0.075	1.195
1:20	1.035	—0.135	1.170	1.08	—0.107	1.187
1:30	1.01	—0.138	1.148	1.05	—0.14	1.190
1:40	0.99	—0.157	1.147	1.033	—0.155	1.188
1:50	0.97	—0.170	1.140	1.02	—0.160	1.180
2:00	0.96	—0.180	1.140	1.008	—0.172	1.180
2:10	0.945	—0.195	1.140	0.995	—0.183	1.178
2:30	0.928	—0.214	1.132	0.975	—0.200	1.175
2:50	0.90	—0.22	1.120	0.95	—0.22	1.170
3:10	0.85	—0.23	1.108	0.91	—0.25	1.160
3:30	0.705	—0.405	1.11	0.81	—0.34	1.150
3:36	0.500	—0.625	1.125	....	——	....
3:40	....	....	....	0:65	—0.51	1.160
3:44	....	....	....	0.50	—0.66	1.160

Table III.

Charging Rate—15 Amperes. Discharging Rate—15 Amperes.
Temperature—70° C. or 158° F.

	Cell A.		CHARGE	*Cell B.*		
Time	Cell Potential in Volts	Potential + Elect. to Test Electrode Volts	Potential — Elect. to Test Electrode Volts	Cell Potential in Volts	Potential + Elect. to Test Electrode Volts	Potential — Elect. to Test Electrode Volts
8:45	1.82	0.06	1.76	1.785	0.075	1.71
8:55	1.855	0.081	1.774	1.823	0.090	1.733
9:05	1.868	0.095	1.773	1.835	0.103	1.732
9:15	1.88	0.104	1.776	1.840	0.110	1.73
9:25	1.88	0.110	1.77	1.840	0.112	1.728
9:35	1.888	0.111	1.77	1.840	0.112	1.728
9:45	1.89	0.119	1.771	1.840	0.120	1.720
10:05	1.89	0.120	1.77	1.840	0.120	1.72
10:25	1.895	0.125	1.77	1.846	0.126	1.72
10:45	1.892	0.123	1.769	1.848	0.128	1.72
11:05	1.89	0.130	1.76	1.848	0.133	1.715
11:25	1.893	0.132	1.761	1.850	0.138	1.712
11:45	1.895	0.133	1.762	1.855	0.141	1.714
12:05	1.895	0.135	1.76	1.855	0.143	1.712
12:25	1.895	0.133	1.762	1.855	0.143	1.712
12:45	1.900	0.140	1.76	1.860	0.142	1.718
			DISCHARGE			
1:00	1.09	—0.06	1.15	1.13	—0.06	1.19
1:10	1.02	—0.095	1.125	1.068	—0.097	1.165
1:20	1.005	—0.122	1.127	1.05	—0.111	1.161
1:30	0.99	—0.130	1.120	1.038	—0.122	1.160
1:40	0.975	—0.140	1.115	1.02	—0.140	1.160
1:50	0.961	—0.154	1.115	1.01	—0.150	1.160
2:00	0.950	—0.167	1.117	1.00	—0.148	1.148
2:20	0.92	—0.170	1.09	0.978	—0.167	1.145
2:40	0.865	—0.216	1.081	0.935	—0.195	1.130
3:00	0.778	—0.300	1.078	0.836	—0.274	1.120
3:05	0.68	—0.410	1.09	0.80	—0.32	1.120
3:08	0.500	—0.595	1.095	....	....	....
3:10	....	....	....	0.67	—0.46	1.130
3:14	....	....	....	0.500	—0.63	1.130

Table IV.

Charging Rate—15 Amperes. Discharging Rate—15 Amperes.
Temperature—80° C. or 176° F.

	Cell A.		CHARGE	*Cell B.*		
Time	Cell Potential in Volts	Potential + Elect. to Test Electrode Volts	Potential — Elect. to Test Electrode Volts	Cell Potential in Volts	Potential + Elect. to Test Electrode Volts	Potential — Elect. to Test Electrode Volts
9 : 30	1.828	0.088	1.74	1.79	0.09	1.70
9 : 50	1.84	0.09	1.75	1.80	0.092	1.708
10 : 10	1.855	0.10	1.755	1.815	0.107	1.708
10 : 30	1.87	0.115	1.755	1.83	0.122	1.708
10 : 50	1.875	0.12	1.755	1.835	0.127	1.708
11 : 10	1.88	0.125	1.755	1.835	0.130	1.705
11 : 30	1.88	0.13	1.75	1.835	0.135	1.70
11 : 50	1.88	0.13	1.75	1.835	0.135	1.70
12 : 10	1.885	0.135	1.75	1.837	0.137	1.70
12 : 30	1.885	0.135	1.75	1.838	0.138	1.70
12 : 50	1.882	0.132	1.75	1.836	0.136	1.70
1 : 10	1.88	0.130	1.75	1.835	0.135	1.70
1 : 30	1.88	0.132	1.748	1.838	0.138	1.70
			DISCHARGE			
1 : 35	1.10	—0.03	1.13	1.14	—0.03	1.17
1 : 55	1.01	—0.11	1.12	1.055	—0.11	1.165
2 : 15	0.978	—0.13	1.108	1.03	—0.128	1.158
2 : 35	0.932	—0.148	1.08	1.007	—0.139	1.146
2 : 55	0.878	—0.150	1.028	0.95	—0.17	1.120
3 : 15	0.84	—0.210	1.05	0.89	—0.210	1.10
3 : 32½	0.500	—0.592	1.092	....	....	....
3 : 35	....	....	....	0.69	—0.41	1.10
3 : 38½	....	....	....	0.500	—0.66	1.16

Table V.

Charging Rate—15 Amperes. Discharging Rate—15 Amperes.
Temperature—90° C. or 194° F.

	Cell A.		CHARGE	*Cell B.*		
Time	Cell Potential in Volts	Potential + Elect. to Test Electrode Volts	Potential — Elect. to Test Electrode Volts	Cell Potential in Volts	Potential + Elect. to Test Electrode Volts	Potential — Elect. to Test Electrode Volts
10:00	1.80	0.08	1.72	1.75	0.095	1.655
10:20	1.815	0.08	1.735	1.762	0.80	1.682
10:40	1.825	0.096	1.732	1.78	0.095	1.685
11:00	1.84	0.108	1.732	1.80	0.11	1.69
11:20	1.85	0.115	1.735	1.805	0.115	1.69
11:40	1.86	1.120	1.74	1.812	0.122	1.69
12:00	1.86	0.128	1.732	1.815	0.125	1.69
12:20	1.86	0.128	1.732	1.817	0.127	1.69
12:40	1.86	0.127	1.733	1.82	0.130	1.688
1:00	1.86	0.130	1.73	1.818	0.131	1.688
1:20	1.86	0.128	1.732	1.818	0.133	1.685
1:40	1.861	0.130	1.73	1.818	0.133	1.685
2:00	1.861	0.131	1.73	1.82	0.134	1.686
			DISCHARGE			
2:05	1.09	—0.02	1.11	1.14	—0.03	1.17
2:25	1.01	—0.07	1.08	1.06	—0.098	1.158
2:45	0.94	—0.088	1.028	1.008	—0.112	1.120
3:05	0.90	—0.10	1.00	0.958	—0.132	1.09
3:25	0.88	—0.125	1.005	0.93	—0.165	1.095
3:45	0.80	—0.24	1.04	0.867	—0.233	1.10
3:50	0.73	—0.300	1.03	0.825	—0.280	1.105
3:54	0.50	—0.528	1.028	....	....	....
3:55	....	....	....	0.77	—0.335	1.105
4:01	....	....	....	0.500	—0.610	1.11

TABLE VI.

Test No.	Cell	Temperature in Degrees C.		Length of Charge Hours	Charging and Discharging Rate—Amps.	INPUT			Time to Reach 0.5 Terminal Voltage	OUTPUT			Current Efficiency in Percent	Energy Efficiency in Percent
		Charge	Discharge			Ampere Hours	Mean Potential on Charge Volts	Watt Hours		Ampere Hours	Mean Potential on Discharge in Volts	Watt Hours		
20	A	20	20	4	15	60	2.1252	127.50	1 hr. 57 min.	29.28	0.7644	45.864	48.8	36.95
	B						2.089	125.24	2 hrs. 2 min.	30.45	0.810	48.60	50.75	38.78
21	A	30	30	4	15	60	2.051	123.06	2 hrs. 12 min.	33.00	0.752	45.12	55.00	36.68
	B						2.018	121.08	2 hrs. 23 min.	35.75	0.839	50.34	59.6	41.55
22	A	40	40	4	15	60	1.994	119.64	2 hrs. 45 min.	41.25	0.824	49.44	68.8	41.33
	B						1.954	117.24	2 hrs. 55 min.	43.70	0.869	52.14	72.8	44.45
23	A	50	50	4	15	60	1.918	115.08	3 hrs. 5 min.	46.3	0.833	49.98	77.7	43.25
	B						1.902	114.12	3 hrs. 9 min.	47.25	0.877	52.62	78.8	46.15
24	A	60	60	4	15	60	1.9046	114.276	2 hrs. 26 min.	36.5	0.9186	55.116	60.85	48.20
	B						1.864	111.84	2 hrs. 34 min.	38.7	0.954	57.24	64.5	51.20
25	A	70	70	4	15	60	1.8812	112.872	2 hrs. 8 min.	32.0	0.9270	55.62	53.35	49.30
	B						1.839	110.34	2 hrs. 14 min.	33.5	0.944	56.64	55.8	51.35
26	A	80	80	4	15	60	1.870	112.20	1 hr. 57.5 min.	29.35	0.918	55.08	49.0	50.00
	B						1.827	109.62	1 hr. 3.5 min.	30.8	0.942	56.52	51.35	51.55
27	A	90	90	4	15	60	1.847	110.82	1 hr. 49 min.	27.25	0.9056	54.336	45.4	49.00
	B						1.803	108.18	1 hr. 56 min.	29.0	0.9672	58.032	48.35	49.12
28	A	80	25	4	15	60	1.8825	112.95	1 hr. 14 min.	18.5	0.728	43.68	30.85	38.68
	B						1.833	109.98	1 hr. 28 min.	21.85	0.7726	46.356	36.40	42.15
29	A	60	25	4	15	60	1.958	117.48	1 hr. 50.5 min.	27.66	0.755	45.30	46.15	38.58
	B						1.899	113.94	2 hrs. 3.5 min.	30.82	0.809	48.54	51.40	42.6
30	A	25	80	4	15	60	2.16	129.60	2 hrs. 39 min.	39.75	0.869	52.14	66.25	40.25
	B						2.103	126.18	2 hrs. 43.5 min.	40.9	0.9466	56.796	72.5	45.00
31	A	25	60	4	15	60	2.135	128.10	2 hrs. 37 min.	39.22	0.8304	49.824	65.36	38.90
	B						2.071	124.26	2 hrs. 38 min.	39.45	0.8780	52.68	65.75	42.40
32	A	80	25	2	15	60	2.030	121.80	1 hr. 31 min.	22.75	0.7712	46.272	37.9	37.95
	B	25		2			1.9712	118.272	1 hr. 52 min.	28.0	0.7996	47.976	46.7	40.55
33	A	40	40	5	15	75	2.039	122.34	2 hrs. 39 min.	39.72	0.8196	49.176	53.00	40.30
	B						1.999	119.94	2 hrs. 44 min.	40.00	0.8556	51.336	53.3	42.80
34	A	30	30	4	15	60	2.103	126.18	2 hrs. 20 min.	35.00	0.7954	47.724	58.3	37.85
	B						2.070	124.20	2 hrs. 27 min.	36.72	0.8364	50.184	61.2	40.38
35	A	25	25	8	15	120	2.1206	254.46	2 hrs. 15 min.	33.75	0.714	42.84	28.13	16.84
	B						2.235	274.20	1 hr. 33.5 min.	23.65	0.7588	48.528	23.65	18.10

Table VI.

Tables I, II, III, IV and V give the data obtained on runs with the temperature varying from 50° C. to 90° C., inclusive (122-194° F.). Table VI contains the condensed results of all test runs with computed efficiencies. The mean cell potentials on charge and discharge of all runs were obtained by ascertaining the mean ordinate of the plotted areas, which were measured by planimeter. Curves shown in Fig. 1 represent the plotted values on discharge recorded in Tables I to V inclusive for cell "A." The upper set of curves illustrate the potential of the iron or negative electrode, the lower set the nickel hydrate or positive electrode, and the middle set the terminal voltage of the cell. It will be noted that there is a falling off in capacity of both the iron and nickel hydrate electrodes upon increasing the temperature.

Reference to Table VI shows that the available capacity of the battery discharged to 0.5 volt increases up to 50° C. (122° F.) after which it falls off. If the capacity at 20° C. (68° F.) be taken as a standard, those following up to 90° C. (194° F.) are open to the criticism that they are all too high. In order to obtain comparable results and such as would correspond to the same relative state of discharge of the cells the capacity should be figured to a voltage higher than 0.5 with increase of temperature.

It is possible to obtain the practical effective resistance (a combination of the true ohmic resistance and polarization) of the cell with increase in temperature by noting the cell potentials corresponding to two values of current flowing and then ascertaining the quotient of the difference in the voltage values by the difference in the current values. In addition to the fact that different results are obtained by this method at different states of discharge of the cell and also depending upon which direction the current flows through the cell (which results in variable polarization effects), the method is based upon the erroneous assumption that polarization is an independent function of the current density. Results, however, obtained by this method show a positive temperature coefficient of cut-off voltage between 20° and 90° C. (68-194° F.) of approximately 0.0014 volts per degree for the size cell under test. Reference to the tables and curves will show that the amount of the correction in the capacities due to decreased resistance of the electrolyte with rise in temperature will be large at lower temperatures and that it will decrease

Table VII.

Charging Rate—15 Amperes. Discharging Rate—15 Amperes.
Charge at 80° C. or 176° F.

Temperature:
Discharge at 25° C. or 77° F.

	Cell A.		CHARGE	*Cell B.*		
Time	Cell Potential in Volts	Potential + Elect. to Test Electrode Volts	Potential — Elect. to Test Electrode Volts	Cell Potential in Volts	Potential + Elect. to Test Electrode Volts	Potential — Elect. to Test Electrode Volts
9:15	1.825	0.110	1.715	1.77	0.020	1.75
:35	1.818	0.088	1.73	1.788	0.058	1.73
:55	1.865	0.125	1.745	1.81	0.125	1.685
10:15	1.885	0.135	1.750	1.829	0.130	1.699
:35	1.90	0.145	1.755	1.845	0.145	1.70
:55	1.90	0.150	1.75	1.850	0.150	1.70
11:15	1.90	0.145	1.755	1.85	0.150	1.70
:35	1.90	0.150	1.75	1.852	0.152	1.70
:55	1.90	0.150	1.75	1.85	0.150	1.70
12:15	1.90	0.150	1.75	1.848	0.150	1.698
:35	1.897	0.147	1.75	1.848	0.151	1.697
:55	1.898	0.153	1.745	1.848	0.158	1.69
1:15	1.895	0.150	1.745	1.845	0.155	1.69
			DISCHARGE			
1:40	0.95	—0.10	1.05	0.975	—0.115	1.09
:50	0.828	—0.202	1.03	0.875	—0.195	1.07
2:00	0.80	—0.22	1.02	0.853	—0.215	1.068
:10	0.772	—0.238	1.01	0.835	—0.235	1.07
:20	0.744	—0.248	0.992	0.81	—0.255	1.065
:30	0.69	—0.28	0.97	0.778	—0.282	1.06
:40	0.622	—0.288	0.91	0.75	—0.302	1.052
:50	0.53	—0.33	0.86	0.69	—0.300	0.99
:54	0.500	—0.345	0.845	....	....	....
3:00	....	....	....	0.595	—0.405	1.00
:08	....	....	....	0.500	—0.490	0.99

Note.—In conjunction with Table VIII this shows how a more effective input into the cells is possible upon lowering the temperature on charge.

with increase of temperature until at 90° C. (194° F.) it is hardly appreciable. This can be observed to be due to the fact that the slope of the cell potential curves near the end of discharge at higher temperatures is much steeper than at lower temperatures. No corrections have been applied to the capacities recorded in Table VI for increased temperatures; the results represent what may be expected commercially.

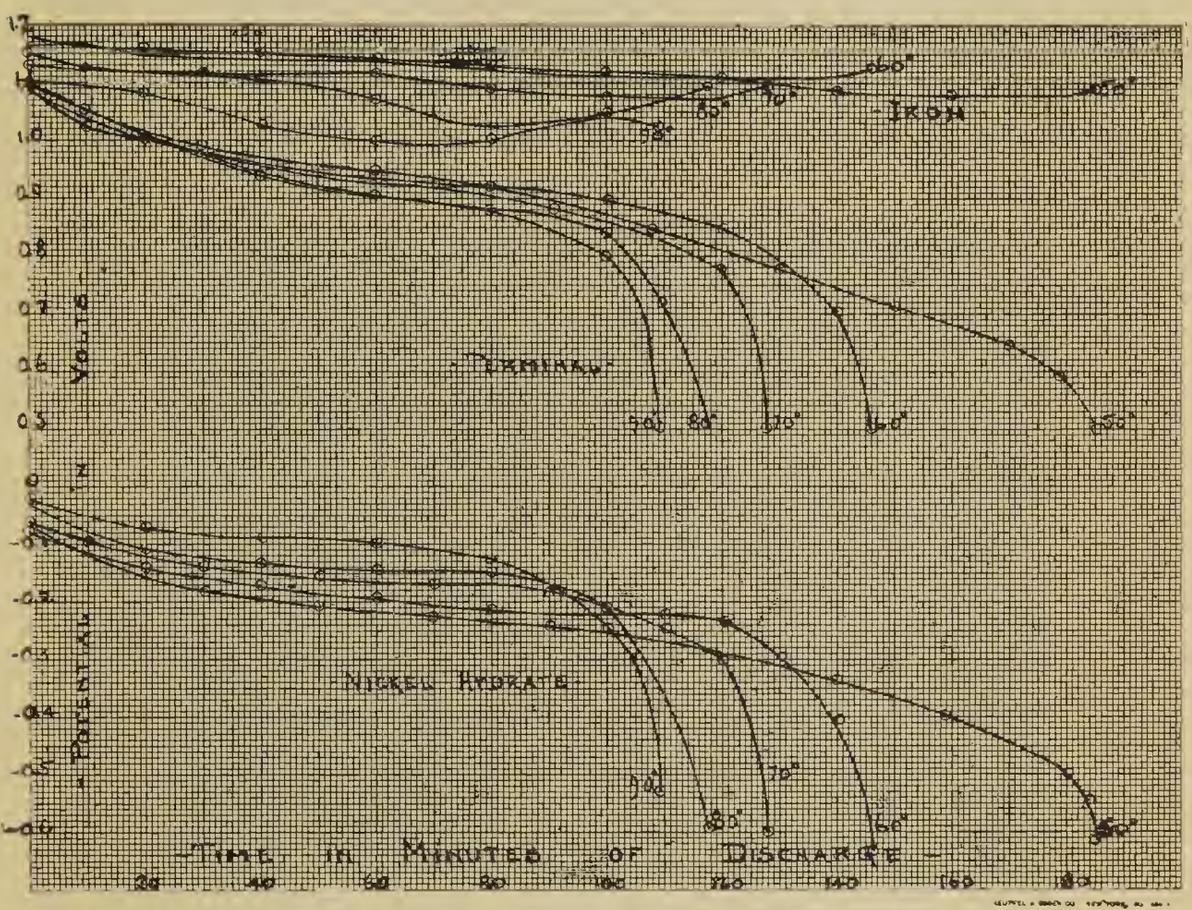

Fig. 1.

Discharge curves showing the effect of temperature upon the capacity and potential characteristics of Cell "A."

Top Group of Curves—Iron electrode potentials.

Bottom Group of Curves—Nickel hydrate electrode potentials.

Middle Group of Curves—Terminal cell voltage.

Cell was charged in each run for four hours at constant temperature and discharged at constant temperature. Charging and discharging rate—15 amperes.

Tests upon the electrolyte made at the different states of charge and discharge of the battery disclose the presence of hydrogen peroxide, which has the peculiar chemical characteristic of being able to function either as an oxidizing or reducing agent. It is known to be able to reduce certain metal peroxides among which is nickel peroxide (NiO_2). The low capacities obtained for the nickel hydrate electrode with increased temperatures as shown

in Fig. 1 is indicative of a low effective input into the battery, which may be explained by the fact that the presence of hydrogen peroxide prevents the formation of additional nickel peroxide. The velocity coefficient for the decomposition of hydrogen peroxide in alkaline solutions is high and has a positive temperature coefficient. It may at first seem improbable that hydrogen peroxide is effecting the reduction of nickel peroxide owing to the fact that the nickel hydrate electrode appears to continue to fall off in capacity with increase in temperature, while the higher the temperature the more rapid the rate of decomposition of hydrogen peroxide in alkaline solutions. While

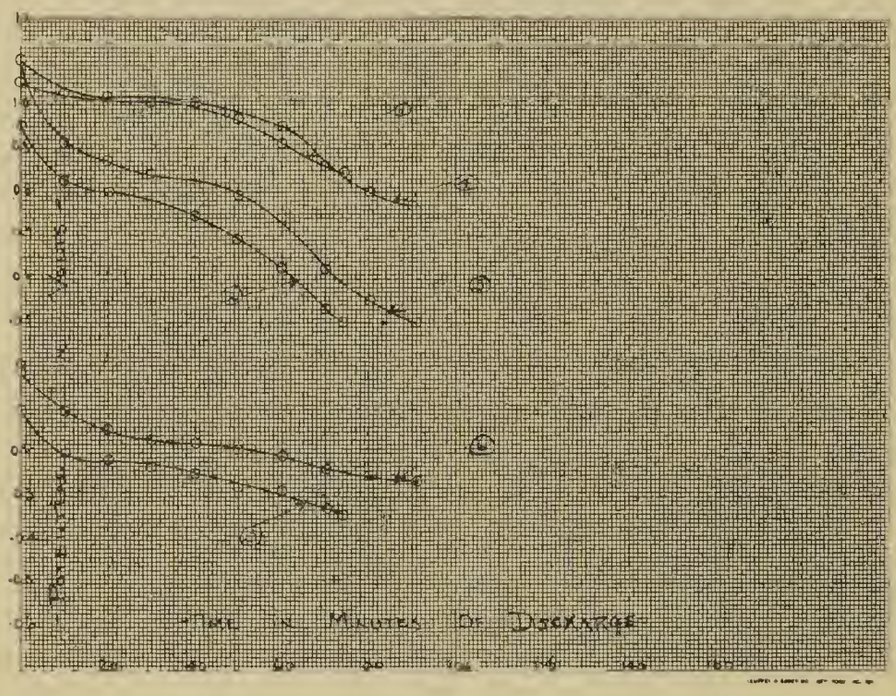

Fig. 2.

Curves 1, 2 and 3 illustrate, respectively, the discharge potentials in Cell "A" of the iron electrode, the terminal voltage, and the potential of the nickel hydrate electrode at 25° C. subsequent to a charge for four hours at 80° C.

Curves 4, 5 and 6 illustrate, respectively, the discharge potentials in cell "A" of the iron electrode, the terminal voltage, and the nickel hydrate electrode at 25° C. subsequent to a charge for two hours at 80° C., followed by an additional charge for two hours at 25° C.

an increase in temperature may affect the amount of hydrogen peroxide present in the electrolyte at any one instant, still the increased rate of decomposition of hydrogen peroxide with rising temperatures does not in any way reduce the velocity of formation of hydrogen peroxide, but, on the contrary, will in all probability increase it. The falling off in capacity of the iron electrode with increase of temperature may be explained by the fact that

Table VIII.

Charging Rate—15 Amperes. Discharging Rate—15 Amperes.
Charge two hours at 80° C. (176° F.) and two hours at 25° C. (77° F.).

Temperature: Discharge at 25° C. (77° F.).

	Cell A.		CHARGE AT 80° C.	*Cell B.*		
Time	Cell Potential in Volts	Potential + Elect. to Test Electrode Volts	Potential — Elect. to Test Electrode Volts	Cell Potential in Volts	Potential + Elect. to Test Electrode Volts	Potential — Elect. to Test Electrode Volts
9:00	1.79	0.08	1.71	1.739	0.094	1.645
:20	1.86	0.108	1.752	1.797	0.122	1.675
:40	1.878	0.123	1.755	1.807	0.122	1.685
10:00	1.895	0.140	1.755	1.826	0.141	1.685
:20	1.907	0.147	1.76	1.84	0.154	1.686
:40	1.907	0.152	1.755	1.84	0.158	1.682
11:00	1.907	0.152	1.755	1.84	0.159	1.681
			CHARGE AT 25° C.			
11:30	2.06	0.210	1.85	2.02	0.240	1.78
:50	2.171	0.285	1.886	2.10	0.295	1.805
12:10	2.17	0.290	1.88	2.10	0.300	1.80
:30	2.18	0.295	1.885	2.12	0.312	1.808
:50	2.20	0.295	1.905	2.155	0.305	1.85
1:10	2.22	0.280	1.940	2.168	0.293	1.87
:30	2.232	0.300	1.932	2.179	0.309	1.87
			DISCHARGE			
1:35	1.10	0.012	1.088	1.13	—0.000	1.13
:45	0.916	—0.109	1.025	0.981	—0.100	1.081
:55	0.875	—0.145	1.02	0.94	—0.140	1.08
2:05	0.84	—0.170	1.01	0.91	—0.165	1.075
:15	0.828	—0.177	1.005	0.90	—0.170	1.07
:25	0.79	—0.195	0.985	0.875	—0.185	1.06
:35	0.74	—0.210	0.950	0.845	—0.195	1.04
:45	0.62	—0.238	0.858	0.767	—0.223	0.99
:55	0.55	—0.250	0.800	0.655	—0.250	0.905
3:05	0.508	—0.262	0.770	0.600	—0.270	0.870
:06	0.500	—0.265	0.765	....	....	....
:15	....	....	....	0.561	—0.284	0.845
:25	....	....	....	0.510	—0.310	0.820
:27	....	....	....	0.500	—0.382	0.812

Note.—In conjunction with Table VII this shows how a more effective input into the cells is possible upon lowering the temperature on charge.

the presence of hydrogen peroxide will have the effect of preventing the reduction of ferrous hydrate to metallic iron on charge.

It is a common observation that the battery continues to give off gas as evidenced by a popping of the valve at the top of the container for a considerable length of time after the cessation of charging. The gas has been found to contain oxygen and it is a fact that the rate of liberation of gases from a charged battery on open-circuit has been found to increase with increase of temperature. The falling off in capacity of the positive electrode upon increase in temperature can be explained by the theory that nickel peroxide (NiO_2) and nickelic oxide (Ni_2O_3) form a solid solution, in which the concentration of NiO_2 in the equilibrium phase decreases with rise in temperature.

Nickel peroxide is decomposed by heat into a lower oxide of nickel with the liberation of oxygen, the process resulting in a loss of current efficiency for the battery.

Reference to test runs Nos. 28 and 32, data of which is shown in Tables VII and VIII and curves in Fig. 2, shows conclusively that a higher effective input in the cell is possible at a lower temperature. At the end of two hours' charge the cell potential as well as each cell electrode appear to have reached a constant value, which would seem to indicate that an apparent state of equilibrium has been attained between reactions causing further oxidation of the positive electrode and reduction of the negative electrode and those having the effect of a reverse nature. The concentration of nickel peroxide in the equilibrium phase of the solid solution with nickelic oxide has reached the maximum possible at that particular temperature; it can be increased only upon lowering the temperature. Test run No. 35, the results of which are recorded in Table IX and the curves on discharge shown in Fig. 3, seems to be further evidence in support of this view.

While cell *B* in test No. 35 was standing on open-circuit for a period of six hours in the bath, which was maintained at 80° C. (176° F.) gas of a very explosive nature was evolved continuously. Analysis of samples showed both hydrogen and oxygen, averaging over ninety percent of the former. The hydrogen no doubt was obtained as a by-product in the solution of the very active iron of the charged negative electrode in the strong caustic

Table IX.

Charging Rate—15 Amperes. Discharging Rate—15 Amperes.
Charging Temperature—25° C. (77°F.).

	Cell A.		CHARGE.	*Cell B.*		
Time	Cell Potential in Volts	Potential + Elect. to Test Electrode Volts	Potential — Elect. to Test Electrode Volts	Cell Potential Volts	Potential + Elect. to Test Electrode Volts	Potential — Elect. to Test Potential Volts
8:00	1.925	0.165	1.76	1.86	0.17	1.69
:20	2.07	0.230	1.84	2.007	0.237	1.77
:40	2.086	0.249	1.837	2.022	0.262	1.76
9:00	2.11	0.270	1.84	2.04	0.279	1.761
:20	2.13	0.284	1.846	2.058	0.273	1.785
:40	2.142	0.284	1.858	2.070	0.290	1.78
10:00	2.155	0.295	1.860	2.08	0.300	1.78
:20	2.17	0.300	1.87	2.10	0.300	1.800
:40	2.20	0.300	1.90	2.133	0.305	1.828
11:00	2.247	0.297	1.95	2.155	0.305	1.850
:20	2.27	0.295	1.975	2.162	0.307	1.855
:40	2.275	0.315	1.96	2.168	0.308	1.86
12:00	2.28	0.292	1.988	2.17	0.310	1.86
:20	2.283	0.293	1.99	2.168	0.308	1.86
:40	2.29	0.290	2.00	2.167	0.304	1.863
1:00	2.29	0.290	2.00	2.165	0.315	1.85
:20	2.29	0.300	1.99	2.165	0.305	1.86
:40	2.305	0.295	2.01	2.167	0.325	1.842
2:00	2.32	0.300	2.02	2.165	0.315	1.85
:20	2.34	0.295	2.045	2.165	0.323	1.842
:40	2.335	0.295	2.04	2.168	0.318	1.85
3:00	2.33	0.300	2.03	2.17	0.320	1.85
:20	2.36	0.300	2.06	2.16	0.320	1.84
:40	2.34	0.300	2.04	2.165	0.321	1.844
4:00	2.335	0.303	2.032	2.165	0.325	1.84
			DISCHARGE			
2:20	1.00	—0.04	1.04	0.94	—0.140	1.08
:30	0.938	—0.102	1.04	0.88	—0.184	1.064
:40	0.90	—0.138	1.038	0.85	—0.200	1.05
:50	0.87	—0.170	1.04	0.813	—0.222	1.035
3:00	0.855	—0.161	1.016	0.79	—0.230	1.02
:10	0.83	—0.178	1.008	0.75	—0.245	0.995
:20	0.815	—0.193	1.008	0.69	—0.265	0.955
:30	0.78	—0.218	0.998	0.62	—0.290	0.910
:40	0.73	—0.225	0.995	0.57	—0.310	0.88
:50	0.672	—0.243	0.915	0.52	—0.325	0.845
3:53½	....	....	....	0.500	—0.327	0.827
4:00	0.645	—0.255	0.90	....	....	....
:10	0.60	—0.270	0.87	....	....	....
:20	0.56	—0.288	0.848	....	....	....
:30	0.526	—0.300	0.826	....	....	....
:35	0.500	—0.312	0.812	....	....	....

Note.—After both Cell *A* and Cell *B* received a charge for eight hours at 25° C. Cell *A* stood on open-circuit for 22 hours at 25° C. while Cell *B* stood on open-circuit for 16 hours at 25° C. and six hours at 80° C. (176° F.) before the beginning of their discharge.

solution, presumably with formation of a ferrite. The electrolyte shows the presence of iron in solution. This, in addition to the fact that ferrous hydrate (the material in a discharged negative electrode) dissolves in hot strong caustic solution forming a ferrite, would account for low capacity iron, which can not be increased with overcharging. The presence of iron in the electrolyte would also result in a lower available current efficiency.

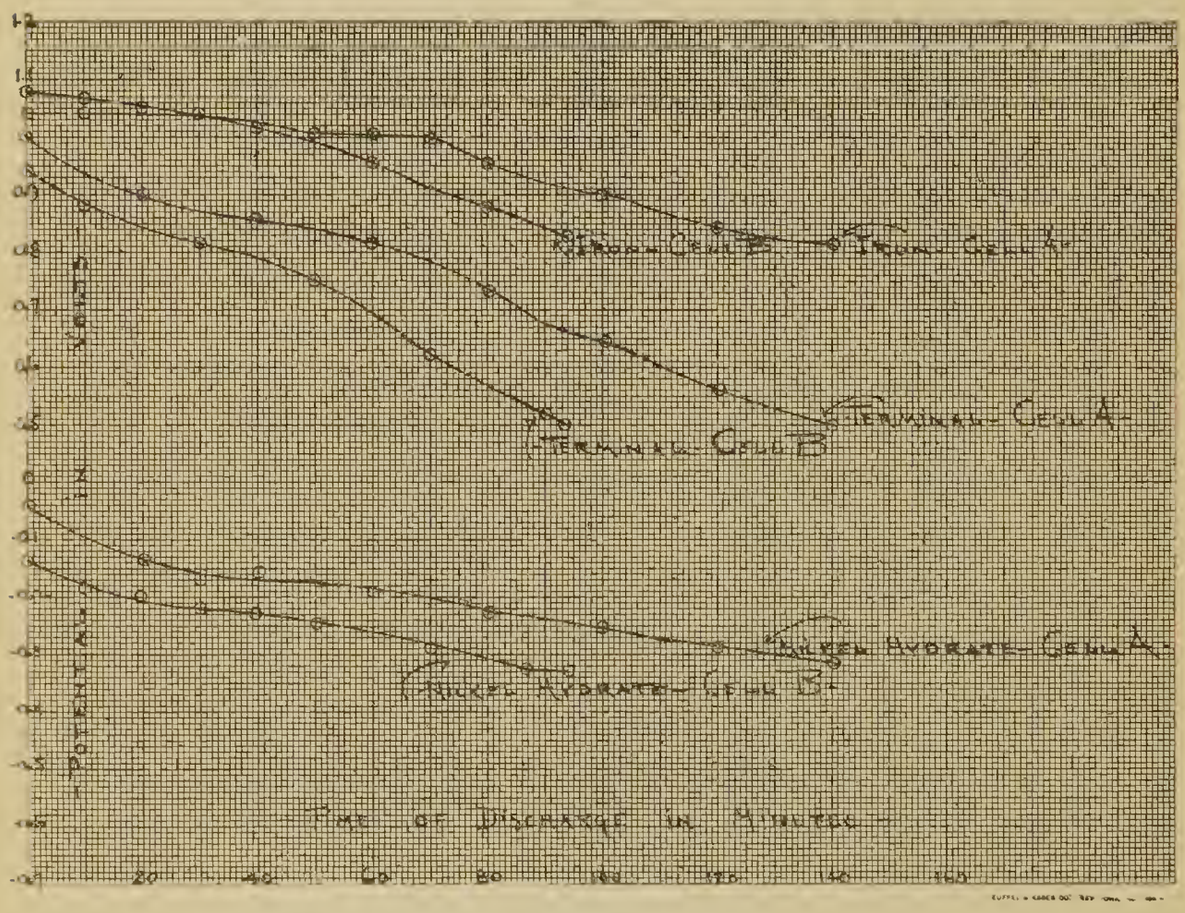

Fig. 3.

Discharge potential curves of cells "A" and "B" subsequent to an eight-hour charge at 25° C.

Before commencement of discharge and after receiving their charge, cell "A" was kept for 22 hours at 25° C. and cell "B" 16 hours at 25° C. and six (6) hours at 80° C. Both were discharged at 25° C. Charging and discharging rate—15 amperes.

The gas liberated from cell *B* in run No. 35 escaped at the rate of over thirteen hundred cubic centimeters per hour for the full six hours that the cell was maintained at 80 degrees. Larger sizes of cells under similar conditions would liberate proportionately larger amounts. Gas evolution was perceptible at 50° C. (122° F.) and the rate increased very rapidly with increase of temperature. Such a large volume of hydrogen coming from cells allowed to overheat, unintentionally or otherwise, and at a time

when perhaps any ventilating system may not be operating in view of the fact that the cells are not charging and are on open-circuit, may account for some of the serious explosions that have been experienced with larger sizes of the battery.

SUMMARY.

1. The available current efficiency of the battery at charge and discharge rates twice the value of the recommended "normal" rates increases up to 50° C. (122° F.), after which it begins to fall off rapidly with further increase in temperature.

2. The current efficiency on discharge is higher than on charge as evidenced by practically no gas evolution during discharge even at rates higher than "normal."

3. A more effective input into the battery is possible by keeping the temperature below 50° C. (122° F.). The best electrical efficiency is obtained by charging at a low temperature and discharging at a higher temperature.

4. The operation of the battery at temperatures above 50° C. (122° F.) is detrimental to the life of the battery. The capacity of the positive or nickel hydrate electrode may be restored by an overcharge at a low temperature. The capacity of the iron or negative electrode will continue to lose in capacity with operation at high temperatures and its lost capacity can not be restored with overcharging.

5. The presence of hydrogen peroxide in the electrolyte during the various states of charge of the battery may account for the low capacities experienced with the battery allowed to operate at high temperatures. On charge it functions as a reducing agent toward the positive electrode and has the effect of an oxidizing agent toward the negative electrode.

6. Another view explaining the low capacity of the positive and negative electrodes, and which the evidence so far obtained seems to support the more strongly, is as follows:

On charge the nickel peroxide (NiO_2) and nickelic oxide (Ni_2O_3) form a solid solution, in which the concentration of NiO_2 in the equilibrium phase decreases with increase in temperature.

The highly active metallic iron of the charged negative plates

is soluble in the electrolyte and the rate of solution increases with increase in temperature. Solution of the iron in the electrolyte results in a permanent loss of capacity.

7. It is dangerous to allow the battery to become overheated and stand even on open-circuit in a place that is not sufficiently ventilated, artificially or otherwise. Evolution of hydrogen and oxygen, in the proper proportion to form in themselves a highly explosive mixture, is evident at 50° C. (122° F.) and the rate increases rapidly with increase of temperature.

The foregoing represents in part results of an extended investigation of the characteristics and behavior of the alkaline storage battery. Additional findings will be given out at a later date.

Carnegie Institute of Technology,
Schenley Park, Pittsburgh.

DISCUSSION.

J. W. Richards: I think we should hear from chemists on the question of hydrogen peroxide acting as a reducing agent in this battery. It sounds paradoxical.

Conclusion No. 7 is as follows: "It is dangerous to allow the battery to become overheated and stand even on open-circuit in a place that is not sufficiently ventilated, artificially or otherwise. Evolution of hydrogen and oxygen, in the proper proportion to form in themselves a highly explosive mixture, is evident at 50° C. (122° F.) and the rate increases rapidly with increase of temperature."

This phenomenon is assuming very great importance in the use of the storage battery in confined places, and has an important bearing on the question of the suitability of this type of battery for use in submarines.

F. C. Frary: It is too bad the author did not extend this investigation to include a lower temperature. Few batteries operated under normal conditions would probably be above 50° C., but a good many of them are put in vehicles and allowed to stand outdoors in the winter, and the question is, what would happen to the capacity of the battery then.

With regard to the hydrogen peroxide, it is well known that hydrogen peroxide will give us oxygen evolution with manganese dioxide or permanganate, in both cases acting as a reducing agent. Several persons working with nickel anodes in caustic solutions have shown, apparently conclusively, that neither ozone nor hydrogen peroxide is formed anodically in appreciable quantity, and since the test which the authors probably used (ether and chromic acid) is very delicate and somewhat uncertain, it would probably be well worth while to have that matter looked into rather more carefully and the details of the test given before such a statement as appears in the paper is generally accepted. Under ordinary conditions you can get solutions that contain a little hydrogen peroxide, and yet give no test; in other cases you may get solutions entirely free from hydrogen peroxide which give the test, from peroxide present in the ether.

It is also possible that a small amount of nickel peroxide, which would undoubtedly be suspended in the electrolyte, would give the same test, because the test is simply the oxidation of the chromic acid to a higher form, which would give the blue color to the ether, and is a very delicate test under proper conditions.

L. C. Turnock (*Communicated*): Adverse criticism as to the probability of hydrogen peroxide being present in the battery was fully anticipated. It would be quite natural to believe it unlikely since hydrogen peroxide is so unstable in alkaline solution. Such a fact, however, is no strong argument against the possibility of hydrogen peroxide being formed in the battery during the various stages of charge and discharge. The suggestion was offered that hydrogen peroxide was the cause of the low capacities experienced with the positive plates at higher temperatures, in view of the fact that tests undoubtedly indicate its presence in the electrolyte. No claim is made for the absolute truth of the statement. Tests reveal but very small quantities, which is entirely in accord with what may be expected in alkaline solution. Any arguments or convincing facts that would tend to discredit the suggestion would be very much appreciated. As stated in Item 6 of the summary of the paper, we believe that the instability of nickel peroxide with rising temperature and the solution of metallic iron in the electrolyte are the more satisfac-

tory explanations of the lowering of the capacities of both the positive and negative plates of the battery with rising temperature. The hydrogen peroxide theory was offered as a second reason, and for the value of any discussion it might bring forth.

In our work covering the electrolysis of caustic solutions with plain nickel electrodes, we have been unable to obtain any indication whatsoever of the presence of either ozone or hydrogen peroxide. Conclusions drawn from such tests, however, and applied to the Edison battery would not be justifiable, since the conditions of such tests are entirely incomparable to those prevalent in the alkaline storage battery. In the first place the plates of the battery are placed mechanically as close together as it is practicable to do so, since the electrolyte resistance is relatively high. On charge, hydrogen and oxygen are evolved in immediate proximity to each other. Secondly, in place of plain nickel electrodes we have, on the one hand, electrodes made up of a probable mixture of nickelous oxide, nickelic oxide, nickel peroxide, and finely divided metallic nickel; and, on the other hand, an electrode composed of a mixture of ferrous hydrate and very finely divided and highly active metallic iron. Some of these constituents are well known for their excellent catalytic effect in certain chemical reactions.

A mistake has been made in the assumption that the ether and chromic acid test was used to determine the presence of hydrogen peroxide. Portions of the battery electrolyte were withdrawn frequently during the various periods of charge and discharge, made acid with sulphuric acid (at all times maintaining a low temperature) and solutions of ferrous sulphate, potassium iodide and starch added successively. Other oxidizing agents have the power of liberating iodine from potassium iodide, but not in the presence of ferrous sulphate. If ozone were formed in the electrolyte and a blue coloration would indicate its presence as well as that of hydrogen peroxide, it is reasonable to believe that the gases evolved from the cells would likewise reveal the presence of ozone, which they do not. The starch iodide test for hydrogen peroxide is claimed to be delicate enough to detect one part in twenty-five million parts of solution.

Another test used in determining the presence of hydrogen peroxide, where it is not necessary to neutralize the alkaline solu-

tion with sulphuric acid, is to add direct to small portions of the electrolyte a few drops of cobalt nitrate. A brownish-black precipitate indicates the presence of hydrogen peroxide in the absence of hyposulphites and sulphides.

In addition to manganese dioxide and potassium permanganate, hydrogen peroxide will reduce silver oxide and lead peroxide. Furthermore, the contents of a tube composing a charged positive plate likewise appear to oxidize hydrogen peroxide.

With reference to Mr. Frary's suggestion that the test should have been carried to a lower temperature, presumably meaning below 50° C., attention is called to Table 6, which shows tests at temperatures down to 20° C. However, instead of showing the effect of low temperatures upon the capacity of the battery, the results above were given to illustrate more specifically how the current efficiency of the battery attains a maximum value at about 50° C., and that either a decrease or an increase in temperature from this value results in a lower current efficiency. Therefore there are shown only records of tests at a sufficient number of temperature values above and below 50° to illustrate this fact. The practical current efficiency, or what would correspond to the available capacity of the battery, will continue to drop with lowering of the temperature below 20° C.

In cold weather the temperature of a working battery is always considerably above that of the outside air, the amount depending upon its rate of discharge, the electrolyte resistance, and how well insulated thermally the battery is from the outside air. Owing to the fact that the Edison cell will radiate heat much more rapidly than the lead storage battery, because of the nature of its container, it is necessary to pay more attention to the proper insulation of the former from the cold. It seems to be a rather fortunate circumstance that the internal resistance of the storage battery increases with lowering of temperature, since the generation of heat within the battery (I^2R loss) increases automatically with decrease of temperature.

With reference to Dr. Richard's statement pertaining to item No. 7 in the summary of the paper, it may be stated further that it is imperative that strict attention should be paid to the ventilating system for Edison batteries which are liable to become unduly warm, independent of the fact whether they are operating

or on open-circuit. In the event the battery is to be employed in confined places, such as in submarines and mine locomotive service, a satisfactory cooling arrangement must also be provided, or there will be not only danger of serious explosions, but the life of the battery will depreciate rapidly. The author's attention has been brought to a case where the operation of a mine locomotive equipped with Edison cells had become so unsatisfactory, and the capacity of the battery had fallen off to such an extent through excessive heating, that it was deemed advisable to replace it long before its life under normal temperature conditions should have been exceeded. Under analogous conditions the amount of internal heating would be considerably less in the lead storage battery than in the Edison, due to the fact that the electrolyte resistance of the former is much less than that of the latter. Data bearing on this subject will be given out shortly.

A paper presented at the Thirtieth General Meeting of the American Electrochemical Society, held in New York City, September 29, 1916. Mr. L. E. Saunders in the Chair.

THE EQUILIBRIUM BETWEEN BROMINE AND POTASSIUM BROMIDE SOLUTIONS AT 0°.

By Grinnell Jones and Miner Louis Hartmann.

The authors of this paper have recently published[1] a study of the influence of temperature on the free energy of formation of silver iodide, a study which revealed suggestive relationships between the thermodynamic properties of this substance, and which furnished a plausible explanation of the negative coefficient of expansion of silver iodide. Since it seemed desirable to test the generality of these relationships by a study of other similar cases, a study of silver bromide was planned. But in order to interpret measurements of the potential of the silver-silver bromide-bromine cell similar to the silver-silver iodide-iodine cells previously investigated, it is first necessary to ascertain the concentration of each of the ions present (Br^-, Br_3^-, Br_5^-, H^+, K^+), and to ascertain also the mobility of each ion. And moreover, since we are concerned with the temperature coefficient of the free energy, we need these data at two or more temperatures, preferably 25° and 0° C. This paper records and interprets the results of our experimental investigations of this preliminary problem at 0°.

Previous Investigations. Winkler[2] found that the vapor pressure of bromine from its solutions in water is proportional to the concentration. This proves that the molecular complexity of bromine in aqueous solution is the same as in the vapor phase, and since bromine vapor is Br_2, therefore bromine dissolves in water as Br_2 also.

M. Wildermann[3] made a single determination of the solubility of bromine in water and in normal potassium bromide at 22° C.,

[1] Jones and Hartmann, Jour. Amer. Chem. Soc., **37**, 752 (1915).
[2] Chem. Zeit., **23**, 687 (1899).
[3] Z. physik. Chem., **11**, 416 (1893).

and also of the vapor pressure of bromine from these solutions. He concluded that bromine dissolves in normal potassium bromide as Br_2 and KBr_3, and that some higher polybromide must also be present, which he assumed to be KBr_5. He found by experiment that 100 moles of liquid bromine dissolve only 0.4 mol. of water at 22° C.

M. Roloff[4] carried out experiments on the distribution of bromine between carbon bisulphide and potassium bromide solutions at 32.6° C. He calculated the equilibrium constant for the formation of KBr_3, namely, $K_3 = \frac{(KBr)(Br_2)}{KBr_3}$. K_3 varied from 0.0480 to 0.0510, but the concentrations of potassium bromide and of bromine were changed only slightly, and the amount of bromine was always much less than sufficient to saturate the solutions, which accounts for the close agreement of his "constant." He took no account of hydrolysis, or the formation of higher polybromides, nor of electrolytic dissociation. Roloff concludes that his results prove the formation of KBr_3 in the solution.

Jakowkin[5] determined the distribution of bromine between carbon tetrachloride and solutions of potassium bromide at 25° C. through a wide range of concentrations of potassium bromide and of bromine, although none of his solutions were saturated with bromine, and calculated the equilibrium constant for the formation of KBr_3 from his results. K_3 varied from 0.06077 to 0.06642. He concluded that the variation in the constant is due to the formation of higher polybromides, probably KBr_5, but made no attempt to determine the amount of this higher polybromide or to apply a correction for its presence. He took no account of hydrolysis.

Bugarsky[6] determined the tri-bromide equilibrium without consideration of any other polybromide, by measurements of the speed of bromination of acetaldehyde. He found $K_3 = 0.0665$ at 25° C., which agrees remarkably well with Jakowkin's value, considering the very diverse methods.

The most extensive study of this problem was made by Worley.[7] He determined the solubility of bromine in water and in solutions

[4] Z. physik. Chem., 13, 341 (1894).
[5] Z. physik. Chem., 20, 19 (1896).
[6] Z. physik. Chem., 38, 561 (1901); 48, 63 (1904).
[7] J. Chem. Soc., 87, 1107 (1905).

of potassium bromide from 0.01 normal up to 0.9 normal at 18.5° and 26.5°. Then he placed water containing bromine in one limb of an inverted U tube and 0.1 *N* KBr containing bromine in the other limb, and rocked gently in a thermostat for about twenty hours. He assumed that during this time the distillation of bromine from one solution to the other would cause the two solutions to have the same vapor pressure of bromine, and hence the same concentration of dissolved Br_2. Then he titrated the bromine in the two solutions and thus found the excess of bromine in the potassium bromide solution, which would be the combined bromine. However, during this process of distilling bromine, there must have been some distillation of water into the potassium bromide solution, causing an indefinite dilution, which was not determined after the experiment.

Like all of his predecessors Worley neglected entirely the hydrolysis of bromine, which, as will be shown later, is quite appreciable in pure water and in dilute potassium bromide solutions. His results on the solubility of bromine in potassium bromide show that in solutions more dilute than 0.1 *N* the excess bromine present over that dissolved by water is about 2 atoms of bromine (1.94 to 2.14) per molecule of potassium bromide, whereas in 0.9 *N* solutions this ratio becomes 2.27. "It appears probable, then, that in very dilute solutions of potassium bromide saturated with bromine practically all of the potassium bromide has united to form KBr_3, and that in more concentrated solutions small quantities of a more complex compound are also formed."

He used his data on unsaturated solutions to compute the equilibrium constant $K_3 = \frac{KBr \times Br_2}{KBr_3}$, and found a regular systematic change in his constant from 0.0296 in the solution containing the most bromine to 0.0620 in the solution containing the least bromine. Then he computed the equilibrium constant $K_5 = \frac{KBr \times Br_2}{KBr_5}$ and found again a systematic change from 0.0330 in the stronger solutions to 0.0028 in the weaker. "The only interpretation that this can have, in accordance with the law of mass action, is that the compound produced is chiefly KBr_3, but that a smaller amount of some more complex compound is also formed." He made no attempt to compute quan-

titatively the amount of KBr, KBr_3, and the higher complex. This conclusion seems to us correct, but it follows that if these solutions which are unsaturated with bromine contain appreciable amounts of some higher complex, *e. g.*, KBr_5, then the saturated solutions must have contained relatively more, and the conclusion which he drew from his work on saturated solutions, that in these solutions the KBr is entirely converted into KBr_3, must be wrong. The saturated solutions evidently contain KBr, KBr_3, and some higher polybromide, perhaps KBr_5, in appreciable quantities, and in such proportions that for every molecule of KBr in the original solution, approximately two atoms of bromine are taken up in making the complexes.

Boericke[8] has also measured the solubility of bromine in water and in potassium bromide solutions up to 3 normal at 0° C. and at 25° C., but used only one strength of solution below 0.1 *N*. This work was followed by measurements of the potential of bromine electrodes. He did not attempt to calculate equilibrium constants from his data. In the calculation of the normal potential of the bromine electrodes he computed the amount of KBr_3 by the use of Jakowkin's value for the equilibrium constant, and ignored hydrolysis and polybromides higher than KBr_3.

Josephs and Jinendradasa[9] have also investigated this problem. From a comparison of the colors of solutions containing different amounts of bromine and of potassium bromide, they were able to draw conclusions in regard to the amount of tribromide formed, and hence to compute the equilibrium constant, and found that K_3, the constant, varies from 0.058 to 0.036. They made no correction for hydrolysis or for the formation of polybromides.

The only determination, which we have found, of the hydrolysis of bromine, according to the equation

$$Br_2 + H_2O = H^+ + Br^- + HBrO,$$

was made by Bray and Connolly,[10] who determined the solubility of bromine in water and the conductivity of the solution at 25° C., and also the conductivity of unsaturated solutions containing known amounts of bromine. They computed the amount of HBr_3 present by using Jakowkin's value of the equilibrium con-

[8] Z. Elektrochem., **11**, 57 (1905).
[9] J. Chem. Soc., **99**, 274 (1911).
[10] Jour. Amer. Chem. Soc., **32**, 937 (1910); **33**, 1485 (1911).

stant, neglecting the presence of higher bromides in the unsaturated solutions. Bray and Connolly could only guess at the mobility of the tribromide ion which is needed in their calculations. They found the hydrolysis constant,

$$K_H = \frac{(H^+)\ (Br^-)\ (HBrO)}{(Br_2)} = 5.2 \times 10^{-9}.$$

According to their experiments and calculations, a saturated solution of bromine in water at 25° C. has the specific conductivity, 727 x 10^{-6}, and the following composition—bromide, 0.37 x 10^{-3} moles per liter; tribromide, 1.21 x 10^{-3}; pentabromide, 0.13 x 10^{-3}; $H^+ = HBrO$, 1.71 x 10^{-3}, bromide as Br_2, 0.2068.

No one of the previous workers has attempted to calculate the equilibrium constant for the formation of pentabromide, or has even attempted to apply a correction for its presence before computing the equilibrium constant for the formation of tribromide, or has allowed for hydrolysis. We were unable to find any data from which the mobility of the tribromide and pentabromide ion could be deduced. Data at 0° C. were especially meager. It thus became apparent that a new experimental study of this problem must be undertaken before the problem in which we were primarily interested could be attacked with hope of success. This paper reports the results which have been obtained at 0° C.

Liquid bromine in the presence of water is in a metastable condition at 0° C., but nevertheless these metastable solutions can be studied successfully, and only a small proportion of our experiments were lost on account of the appearance of a solid hydrate,[11] which is the stable form below 6.2° C.

A study of the available literature, together with some preliminary measurements of our own, made it evident that the equilibrium between bromine and potassium bromide solutions is a very complex one. There is evidence that all of the following processes occur simultaneously.

1st. Bromine dissolves as Br_2 in considerable amounts (more than 0.2 moles per liter).

2d. Bromine reacts with water, according to the reaction

$$Br_2 + H_2O \leftrightarrows H^+ + Br^- + HBrO.$$

[11] This hydrate has the formula $Br_2.10H_2O$, according to Roozeboom, Rec. Trav. Chim. Pays-Bas, **4**, 65, and $Br_2.8H_2O$, according to Giran, Compt. rend., **159**, 246.

3d. There is much evidence that the reaction $KBr + Br_2 \leftrightharpoons KBr_3$ occurs to a large extent.

4th. The three processes described above are not sufficient to account for the large solubility of bromine in potassium bromide solutions, so that it is necessary to assume that still more complex polybromides are formed. Most investigators assume that the compound KBr_5 is formed. No quantitative evidence for this formula of the complex has been offered. The assumption of this formula is based on the fact that bromine exists in solution as Br_2, and therefore the simplest assumption is that the reactions, $KBr + Br_2 = KBr_3$ and $KBr + 2Br_2 = KBr_5$, occur. This is supported by the fact that a solid compound of this type, *e. g.*, $CsBr_5$,[12] has been prepared.

There are two other possible reactions which should be considered, namely,

$$3H_2O + 3Br_2 \leftrightharpoons 6H^+ + 5Br^- + BrO^-_3$$
$$2H_2O + 2Br_2 \leftrightharpoons 4H^+ + 4Br^- + O_2.$$

Bromate will be formed in considerable quantities, if bromine is added to potassium hydroxide until the solution is neutralized, and then the solution heated. In the presence of acid or bromides the reaction goes very nearly to completion in the reverse direction. Bray and Connolly disregarded this reaction in the computation of the equilibrium, $H_2O + Br_2 \leftrightharpoons H^+ + Br^- + HBrO$ at 25° C., and their result is quoted and used by Skrabal,[13] who has done extensive work on the kinetics of this reaction and other reactions involving the formation and decomposition of bromates. The formation of bromates is a very slow one and is undoubtedly much slower at 0° than at 25°, and there is probably less formed at equilibrium than at 25°.

It is well known that chlorine will liberate oxygen from water in the presence of sunlight, but the reaction is a slow one. When hydriodic acid is exposed to air and sunlight, the iodine is liberated. Calculations based on the existing very unsatisfactory data regarding the potential of the bromine and oxygen electrodes indicated that bromine is a powerful enough oxidizing agent to liberate oxygen from water. These calculations indicate nothing in regard

[12] Wells and Wheeler, Z. anorg. Chem., **182**, 97.

[13] Skrabal and Weberitsch, Monatshefte der Chemie, **36**, 245.

to the speed of the reaction. We exposed an inverted test-tube containing 15 c.c. of saturated bromine water to direct sunlight for several weeks at room temperature. A small bubble of gas, about 0.1 c.c., collected in the top of the tube, but it could not be determined whether this bubble was oxygen or simply dissolved air coming out of solution by variations in room temperature. This experiment, however, demonstrated that this reaction is an exceedingly slow one, even at room temperature and it is to be expected that it would be still slower at 0° C.

This reaction or the reaction involving the formation of bromate may, however, be responsible for a difficulty which we encountered in the measurement of the conductivity of these solutions. In all the measurements of conductivity of solutions of bromine in water and in dilute potassium bromide solutions, we observed that the conductivity increased continuously and steadily, and did not reach a maximum value even after many hours. This phenomenon was more pronounced in solutions of bromine in water than in the dilute potassium bromide solutions, and disappeared entirely in the stronger potassium bromide solutions which we used. The phenomenon was more pronounced in the cell in which the electrodes were about 1 mm. apart than in the cell in which the electrodes were about 1 cm. apart. When the solution in the conductivity cell was replaced by some of the original solution, the conductivity returned to its original value. These facts indicate that the increased conductivity is due to the reaction, $2H_2O + Br_2 = 4HBr + O_2$, or $3H_2O + 3Br_2 = HBrO_3 + 5HBr$, or both, the speed of the reactions being inappreciable in the original bottle in which the solution was prepared, but acquiring an appreciable velocity in the conductivity cell, owing to the catalytic effect of the electrodes, which were made of platinum-iridium alloy coated with spongy iridium. In order to test this hypothesis further, we prepared a conductivity cell in which the electrodes were made of smooth platinum-iridium without the spongy coating of iridium. In this cell the increase in the conductivity with time occurred at a much slower rate. We, therefore, decided to accept the results for conductivity obtained by allowing only sufficient time after filling the conductivity cell for the temperature to become constant. The results obtained in this way were more definite

and reproducible than we could obtain in any other way. Bray and Connolly have made similar measurements at 25° C., but do not mention any change of conductivity with time, although in some experiments which we carried out at 25°, we found the change in conductivity to be even more rapid than at 0° C. It seemed probable that neither of these reactions occurs with appreciable speed at 0° C. in the absence of a catalyst. We, therefore, decided to attempt to secure a quantitative interpretation of the results on the assumption that neither oxygen nor bromate is formed in appreciable amounts under the conditions of our experiments.

We, therefore, adopted as a working hypothesis the assumption that the following reactions occur and none other,

1st. Solubility of bromine in water as Br_2.

2nd. $Br_2 + H_2O \leftrightarrows H^+ + Br^- + HBrO$.

3rd. $KBr + Br_2 \leftrightarrows KBr_3$.

4th. $KBr + 2Br_2 \leftrightarrows KBr_5$.

In addition, we assume that the degree of dissociation of KBr_3 and KBr_5 is the same as the degree of dissociation of KBr. This assumption may be regarded as a very probable one by analogy with the cases of KI and KI_3, which have been proven to have the same degree of dissociation.[14] This assumption also corresponds with what is known in regard to the ionization of salts in mixtures.[15]

Hypobromous acid is known to be an extremely weak acid, and therefore we assume that it is completely undissociated. We have also assumed that the hydrobromic acid produced by hydrolysis is completely dissociated. This is probably true within the limit of experimental error. To attempt to allow for the slight amount of undissociated HBr would add further mathematical complications to a problem which already taxes our mathematical ingenuity and patience.

The problem may be stated as follows: If we add a known amount of bromine to a potassium bromide solution of known concentration, is it possible to determine quantitatively the extent to which each of these reactions will occur? Can we assign values

[14] Bray and Mackay, Jour. Amer. Chem. Soc., **32**, 914 (1910).
Jones and Hartmann, Jour. Amer. Chem. Soc., **37**, 241 (1915).

[15] Bray, Jour. Amer. Chem. Soc., **33**, 781 (1911).

to the concentrations of each molecular species present which are consistent with all the known facts in regard to these solutions, and which at the same time give values for the equilibrium constants of these reactions, which are reasonably constant in spite of considerable variations in the concentration of the potassium bromide and bromine, and which show no systematic variation with the concentrations of the different components?

If this does not prove to be possible, some other assumptions must be made in regard to the mechanism of the reaction. If, however, the attempt is successful, the way is opened for important advances. By measuring the conductivity of the solutions, the mobility of the tribromide and pentabromide ion can be determined, since the mobility of the other ions present is known. We shall then be in a position to determine the normal potential of the bromine electrode, and hence the free energy of reactions involving bromine. We are especially interested in the free energy of formation of silver bromide, and propose to take this case up first, but the possibilities are obviously far wider than this.

Outline of the Plan of the Investigation.—It was first necessary to determine the conductivity of a series of potassium bromide solutions of known concentration varying from 0.1 N down to 0.001 N (see Table I), in order to determine the degree of ionization of potassium bromide and the equivalent conductivity of the bromide ion at 0°.

In order to get the value of the hydrolysis constant,

$$K_H = \frac{(H)\ (Br)\ (HBrO)}{(Br_2)} = \frac{(H)^2\ (Br)}{(Br_2)},$$

we chose the conditions of experiment in such a way that the hydrolysis was at a maximum and the formation of tribromide and pentabromide at a minimum. This was accomplished by adding bromine to pure water, maintaining the solution at 0° until the reaction, $Br_2 + H_2O \leftrightarrows H^+ + Br + HBrO$, proceeded to an equilibrium, then measuring the specific conductivity of the solution and determining the total bromine dissolved by titration. (See Table II). A series of such experiments was made, in

which the bromine varied from a very dilute solution up to saturation. The data for the solubility of bromine in water after correction for hydrolysis gave the solubility of bromine as Br_2.

We now chose the conditions so that the amount of tribromide formed would be relatively large and the hydrolysis and pentabromide relatively small. The formation of tribromide was favored and hydrolysis repressed by using solutions of potassium bromide instead of water. The pentabromide was kept low by using only small amounts of bromine. Since the solutions were not saturated, it was necessary to determine the concentration of the Br_2 by distribution experiments with carbon tetrachloride. We, therefore, shook a series of potassium bromide solutions of known strength with carbon tetrachloride and with an amount of bromine insufficient to produce saturation. After equilibrium had been established we determined the concentration of the total dissolved bromine in each phase. The conductivity of the aqueous solution was also determined in order to furnish data from which the mobility of the tribromide ion could be deduced (see Table IV). In order to interpret these results, it was necessary to determine the distribution ratio of bromine between carbon tetrachloride and water (see Table III).

It now remained to favor the formation of pentabromide by working with solutions of potassium bromide which were saturated with bromine. A series of potassium bromide solutions of known strength were saturated with bromine, and then the conductivity was measured and the total dissolved bromine determined by titration (see Table V). It was not necessary to use carbon tetrachloride in this case, because the concentration of the Br_2 was known from the experiment on the solubility of bromine in water. The data for the conductivity make possible an estimate of the mobility of the pentabromide ion.

In each series the conditions are so chosen that one reaction is made prominent and the other reactions repressed as much as possible. Nevertheless, the secondary reactions do occur, and proper allowance must be made for them in interpreting the results. The mathematical details of these calculations and the conclusions drawn from them will be given after describing the experimental methods and presenting the results.

Experimental Part.

PURIFICATION OF MATERIALS USED.

Water. All the water used in this work was "conductivity water," distilled especially for the purpose. The specific conductance at 0° C. of the water varied from 0.3×10^{-6} to 0.7×10^{-6}.

Potassium Oxalate. Merck's best product was recrystallized until it gave no chloride reaction and showed no indications of impurity when examined in the spectroscope.

Bromine and Potassium Bromide. C. P. bromine was dissolved in a solution of potassium bromide and then distilled in an apparatus constructed entirely of glass. A part of this bromine was converted into potassium bromide by reaction with potassium oxalate which had been purified by crystallization until free from chloride. The remaining bromine was distilled a second time from this purified bromide. The bromine thus obtained must have been free from chlorine, which is the impurity most likely to be present, and the impurity whose presence would be most harmful for the subsequent work. A part of this pure bromine was converted into bromide by means of purified potassium oxalate, and the potassium bromide formed was crystallized, drained centrifugally, and dried in a vacuum desiccator. A slight excess of bromine was used in order to liberate any iodine which might be present, but there was no indication of the presence of iodine. The solution was boiled to drive off the free bromine, and concentrated until the potassium bromide crystallized on cooling. The remaining bromine was dried by shaking several times with concentrated sulphuric acid, and then redistilled under reduced pressure in a sealed glass apparatus. Another sample of bromine was distilled only once from a bromide, but gave results which appeared to be identical with those of the doubly distilled sample.

Carbon Tetrachloride. Of the ordinary organic solvents which might be used for distribution experiments with bromine, carbon tetrachloride dissolves the least amount of bromine and is the most inactive chemcially. Jakowkin[16] tried carbon bisulphide, bromoform, and carbon tetrachloride, and he recommends the latter. Merck's purest carbon tetrachloride, free from sulphur

[16] Jakowkin, Z. physik. Chemie, **18**, 588; **20**, 37.

compounds, was shaken at room temperature with water for some time. The two liquids were separated and the water gave no reaction for chlorides or sulphates, and was perfectly neutral. The carbon tetrachloride was fractionated and the middle portion boiling at constant temperature was collected. After shaking some of this product with water for two hours at 0°, the specific conductivity had only changed from 0.5 to 1.9 x 10^{-6}. Shaking water alone sometimes made as large a change in the conductance, so that this product was assumed to be pure enough.

New carbon tetrachloride was used in each experiment. It was found in some later work that the carbon tetrachloride which was recovered from previous experiments was contaminated by some easily hydrolyzed compound, evidently of bromine. Fractional distillation of a large amount of recovered carbon tetrachloride gave a small fraction with a higher and inconstant boiling point, which gave off free bromine when exposed to air. When this fraction was shaken with water, it gave a large increase in the electrical conductivity of water, which indicated that the bromine compound which was formed was more easily hydrolyzed than carbon tetrachloride. The amount of this bromine compound in our accumulated carbon tetrachloride residues was too small to make possible a more definite identification or a quantitative determination of the amount produced. Carbon tetrachloride, however, was far more inert than any other solvent which we were able to find.

The only way to eliminate this source of error entirely would seem to be to use an indifferent gas in place of a liquid solvent. This would, however, require the development of a new and more troublesome experimental technique. Unfortunately, this attack on carbon tetrachloride by bromine was not discovered until after many measurements had been made at 25°. In some of these we used carbon tetrachloride which had been used once and recovered. The presence of this bromine compound in the carbon tetrachloride was discovered only when recovering some carbon tetrachloride which had stood for weeks in contact with free bromine in our residue bottles. It seems probable that the amount of this substance formed during the few hours required for an experiment would be negligible. In view of the fact that much work had been

done with carbon tetrachloride, and our experience indicated that when fresh carbon tetrachloride was used, the error introduced by this reaction was less than other unavoidable errors, we decided to continue its use. All the results obtained with recovered carbon tetrachloride were rejected, since the presence of this impurity would probably change the distribution coefficient of bromine, and make the conductivity data uncertain, owing to the greater ease of hydrolysis of this substance. The rejection of these data leaves an incomplete series of data for 25° C., which makes it impossible to interpret the remaining data, and time was lacking to repeat them. Moreover, the work done at 25° C. was carried out before the work at 0° C., so that the experimental technique was not so well developed. We have, therefore, decided not to publish any of the data obtained at 25° C. until the whole can be checked by a new experimental investigation.

None of the previous investigators appear to have noticed this reaction between bromine and carbon tetrachloride. Perhaps it occurs only in the presence of the substances used during the titration (free iodine, arsenite, etc.) which may act as carriers or catalytic agents.

Experimental Methods. The potassium bromide solutions were in all cases made up by weight, corrected to vacuum. A tenth normal solution was made up from the salt, and this solution diluted by weight as needed for the other solutions.

The most difficult experimental problem of this investigation was the quantitative manipulation of solutions containing bromine, without loss of bromine vapor. The vapor pressure of bromine is so large that special apparatus had to be devised and the details of manipulation perfected.

The problem was solved after many failures by the simple device diagrammed in the accompanying figure, which seems to fulfill the requirements satisfactorily.

The potassium bromide solution and bromine (and carbon tetrachloride in some cases) were placed in the funnel *A*, which was closed with an ordinary stopper, protected by a rubber cap, and the whole shaken in a mixture of ice and water until saturated. The funnel was then placed upright with only the neck projecting out of the ice bath, the stopper removed and the delivery device

T quickly inserted in its place. The whole was then lifted, inverted and a mixture of ice and water poured around the funnel *A*. The aqueous layer above the bromine could then be withdrawn through *S* into a weighed flask for analysis. The conductivity cells and the pycnometer were filled in a similar fashion. In case both carbon tetrachloride and aqueous layers were to be analyzed, the carbon tetrachloride was drawn off first until the boundary between the two phases was on the level of the delivery tube. The whole was then tilted slightly, bringing the carbon tetra-

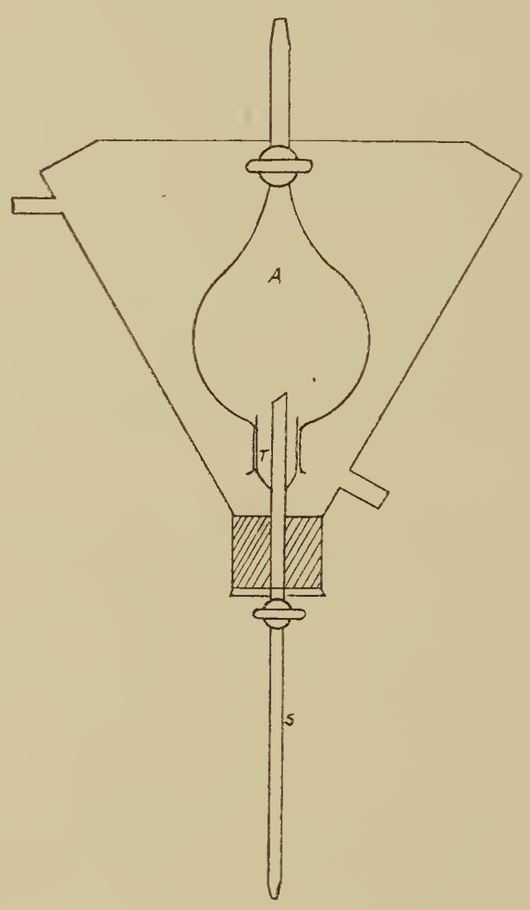

Fig. 1.

chloride layer safely below the level of the delivery tube and the aqueous layer drawn off. In working with solutions saturated with bromine it is very important to avoid even a momentary rise in temperature because bromine is less soluble at the higher temperature and very quickly precipitates out if the solution is warmed.

A *U* tube containing glass pearls was attached to the stem of the separatory funnel when the solutions were being withdrawn through *S*. Some of the solution containing bromine under in-

vestigation was put into the *U* tube, so that the air which entered the funnel, having taken up bromine vapor by bubbling through some of the same solution, would not remove bromine from the solution in the separatory funnel. This device was found to be essential in some determinations made at 25°, and it was continued in the 0° work.

Method of Analysis. The method used to determine the amount of bromine in the solutions was to introduce a weighed quantity of the solution into an excess of concentrated potassium iodide solution, and then to titrate the liberated iodine by means of the sodium arsenite solution containing monosodium phosphate and disodium phosphate in the proportions recommended by Washburn.[17]

Glass stoppered Erlenmeyer flasks containing an excess of strong potassium iodide solution were weighed. By means of the attachment which has been described, samples were then drawn out of the separatory funnel in which the solution had been shaken. The tube *S* was put down into the flask to within one centimeter of the surface of the potassium iodide solution, and some of the bromine solution was allowed to run into it. Iodine was liberated and remained dissolved in the excess of iodide. The flask was stoppered and when it had warmed to room temperature was weighed again, thus determining the weight of the sample of bromine solution taken. The titrations were made by means of weight burets in exactly the same way as in the iodine work. The sodium arsenite solution was standardized against dry iodine.

The apparatus enabled us to handle the bromine solutions quantitatively. Duplicate samples gave analyses agreeing within one-tenth of one percent. Previous investigators of similar problems involving bromine solutions have apparently been satisfied with results agreeing within one-half of one percent.

Density Measurements. Density determinations were made with the modified pycnometers of the Ostwald-Sprengel type.[18]

The Conductance Measurements. The conductance cells were of the pipet type. The electrodes in the conductance cells in the bromide work were made of platinum-iridium (20 percent Ir)

[17] Washburn, Jour. Amer. Chem. Soc., **30**, 31 (1908).
[18] Jour. Amer. Chem. Soc., **37**, 244.

especially for this work. This alloy is very resistant to bromine solutions. The surfaces were covered with iridium black by electro-deposition. A concentrated bromine solution was kept in one of the cells for several days, and the solution was tested for platinum and iridium, but none was found.

In order to determine the effect on the conductivity of shaking with carbon tetrachloride, some experiments were made in which carbon tetrachloride and water or potassium bromide solutions were shaken together without bromine, the conductivity being measured before and after shaking. We expected that if there were any change, it would be in the direction of an increased conductivity, because of dissolved alkali from the glass, the absorption of CO_2 from the air, and perhaps hydrolysis of carbon tetrachloride ($CCl_4 + 2H_2O = CO_2 + 4HCl$?). When water was shaken alone a slight increase (1.4×10^{-6} in one case, and 3.0×10^{-6} in another) was observed, but when potassium bromide solutions were used, we found a decrease in conductivity, in spite of the influences which tend to increase the conductivity. A solution of approximately 0.002 *N* decreased in specific conductivity from 160×10^{-6} to 159×10^{-6}. A solution approximately 0.03 *N* decreased by 9×10^{-6}, or about 0.4 percent, and a solution about 0.2 *N* decreased by 39×10^{-6}, or about 0.3 percent. We found that this decrease in conductivity was not due to the extraction of potassium bromide from the aqueous solution by the carbon tetrachloride, for no residue remained on evaporation of a large volume of carbon tetrachloride which had been shaken with potassium bromide solution.

According to the measurements of A. Rex[19] 0.97 grams of carbon tetrachloride will dissolve in 1000 grams of water at 0°. Since the dielectric constant of carbon tetrachloride is very low (about 2) compared to water (88), it seems probable that the presence of dissolved carbon tetrachloride lowers the dielectric constant of the solution, and hence decreases the ionizing power of the solvent, and therefore decreases the degree of ionization of the salts present. This seems to be the most plausible explana-

[19] Z. phys. Chem., **55**, 365 (1906).

tion of the decrease in conductivity on shaking with carbon tetrachloride. If this be the true explanation of the decrease in conductivity on shaking with carbon tetrachloride, it seems probable that bromine itself has a similar effect to an even greater extent, owing to its greater solubility. We have therefore not attempted to apply a correction to our results on the conductivity of solutions containing bromine which had been shaken with carbon tetrachloride. Perhaps further light could be thrown on this question by measurements of dielectric constants, but both time and equipment for this work were lacking. We must therefore recognize some uncertainty in the assumption that the degree of ionization of the polybromides is the same as that of potassium bromide itself at equivalent concentration, an assumption which we found it necessary to use in order to make any progress toward a quantitative interpretation of our data.

The Experimental Data.

The experimental data are presented in the following five tables:

1. Conductivity and ionization of potassium bromide solutions.

2. Composition and conductivity of dilute bromine water solutions up to saturation.

3. Distribution of bromine between water and carbon tetrachloride.

4. Composition and conductivity of potassium bromide solutions not saturated with bromine and the distribution of bromine between these solutions and carbon tetrachloride.

5. Composition and conductivity of potassium bromide solutions saturated with bromine.

1. *The Conductivity of Potassium Bromide Solutions.* The conductivity of potassium bromide solutions from 0.1 N to 0.0005 N has been carefully determined, and the results are shown in Table I.

TABLE I.

Conductivity of KBr Solutions at 0° C.

Weight Normality	Density 0°/4°	Volume Normality	$\kappa \times 10^6$ Corrected for Water	Conductance Λ	$\frac{100\Lambda}{\Lambda_0} = \gamma$
0.10000	1.0088	0.10088	7378.9	73.15	87.3
0.049998	1.0044	0.050218	3775.9	75.19	89.7
0.019991	1.0017	0.020025	1553.9	77.60	92.6
0.009995	1.0008	0.010003	793.4	79.32	94.7
0.005079	1.0004	0.005081	407.9	80.28	95.8
0.001905	1.0002	0.001906	155.45	81.56	97.4
0.0009916	1.0000	0.0009916	81.38	82.07	98.0
0.0004836	1.0000	0.0004836	40.03	82.78	98.8
0.0000000				83.8	

The value of the conductance at infinite dilution, Λ_0, was found by plotting $1/\Lambda$ against the corresponding values of $(C\Lambda)^{n-1}$ as proposed by A. A. Noyes.[20] This was done for the four solutions from .01 to .001 normal, using $n = 1.45$, which gave the best straight line. The curve was plotted on a large scale, and the best straight line was also calculated by the method of least squares. The 0.0005 normal solution was not used, because the water correction amounts to one percent, and the result is thus too uncertain to be of value in determining the Λ_0 value. In the plot, it fell considerably below the accepted straight line. The application of the method of least squares also showed that the sum of the squares of the deviations from a straight line was much greater when this weakest solution was included.

Graphical extrapolation to infinite dilution gave $\Lambda_0 = 83.82$, while the calculation by the method of least squares gave 83.75. The value 83.8 is accepted and used in all the following calculations.

The data have not been corrected for the viscosity of the solutions, as time and equipment were not available for making these measurements.

If Λ_0 for K^+ be taken as 40.1, Λ_0 for the bromide ion is 43.7.

[20] Jour. Amer. Chem. Soc., **31**, 745 (1910).

Table II.

Solubility of Bromine in Water and Conductivity of the Saturated Solution.

	R	$\kappa \times 10^6$
	0.2564	295
	0.2560	
	0.2560	285
	0.2562	285
	0.2567	281
Mean	0.2563	286

Unsaturated Solutions.

0.1295	177
0.08919	144
0.06940	124
0.017817	67
0.01242	57

The density of a saturated solution of bromine 0°/4° was found to be 1.0286.

Table III.

Distribution of Bromine between Water and Carbon Tetrachloride.

Gm. Br_2 per gm. CCl_4 solution	Density CCl_4-Br_2	C	R
0.1646	1.7667	1.8194	0.07015
0.08661	1.7012	0.9218	0.03937
0.08162	1.6972	0.8666	0.03771
0.07261	1.6896	0.7676	0.03344
0.06126	1.6809	0.6442	0.02870
0.05433	1.6755	0.5695	0.02572
0.01847	1.6470	0.1903	0.00901
0.01640	1.6454	0.1687	0.008007

C = moles Br_2 in carbon tetrachloride per liter.

R = moles free bromine calculated as Br_2 in water per liter.

Table IV.

Potassium Bromide Solutions not Saturated with Bromine at 0° C.

Potassium Bromide Solution		KBr Sol. Partly Sat. with Bromine				CCl_4-Br_2 Sol.	
Weight Normal	Specific Conductance $\kappa \times 10^6$	Vol. N. after sat.	Titrated Bromine Mol./Li.	Specific Conductance $\kappa \times 10^6$	Density 0°/4°	Moles Br_2 per Liter	Density 0°/4°
0.09997	7378.4	0.10054	0.08070	6603.	1.0186	0.8278	1.6943
0.04915	3718.4	0.049189	0.06209	3290.	1.0117	0.9124	1.7004
0.04915	3718.4	0.049306	0.03239		1.0084	0.4083	1.6635
0.01986	1541.2	0.019889	0.01735	1475.	1.0042	0.2854	1.6542
0.01986	1541.2	0.019881	0.01851	1441.	1.0041	0.3053	1.6558
0.009994	789.0	0.009995	0.01533	757.	(1.0026)	0.2887	1.6545
0.009994	789.0	0.009995	0.013595	765.	(1.0023)	0.2519	1.6517
0.004998	401.5	0.0049968	0.015304	396.	(1.0021)	0.3064	1.6558
0.004998	401.5	0.0049956	0.019652	393.	(1.0026)	0.4030	1.6631
0.001964	159.7	0.0019628	0.019604	180.	(1.0024)	0.41845	1.6642

Table V.

KBr Solutions Saturated with Bromine at 0° C.

KBr Solutions			Solutions Saturated with Bromine			
Weight Normal	Volume Normal	Specific Conductance $\kappa \times 10^6$	Volume Normal	Specific Conductance $\kappa \times 10^6$	Density 0°/4°	Titrated Moles Bromine per Liter
0.09909	0.09996	7315.7	0.09819	5491.	1.0502	0.3736
0.05155	0.05178	3874.7	0.05102	2943.	1.0400	0.3149
0.02000	0.020034	1585.0	0.019766	1272.	1.0327	0.2779
0.009003	0.009010	714.8	0.008899	....	[1.0309]	0.2656
0.009611	0.009619	756.0	0.009499	665.	[1.0309]	0.2661
0.002877	0.002877	232.5	0.002842	330.	[1.0296]	0.2586
0.100000	0.10088	7374.	0.09906	5520.	1.0509	0.37344
0.049995	0.05022	3776.5	0.04947	2853.	1.0395	0.31274
0.020045	0.02008	1551.	0.019815	1228.	1.0327	0.27757
0.010022	0.010030	790.0	0.009905	680.	[1.0309]	0.26665
0.0049995	0.005002	403.0	0.004941	431.	[1.0299]	0.26054
0.0019997	0.002000	[163.1]	0.001976	299.	[1.0294]	0.25774
0.0009987	0.000999	[82.1]	0.000988	278.	[1.0292]	0.25698

When bromine dissolves in potassium bromide solutions the volume of the solution increases. The change concentration due to this increase in volume has been calculated by the aid of the density and concentration of the solutions. The corrected concentration is recorded in the fourth column of Table V and in the third column of Table IV.

The Interpretation of the Results by the Method of Successive Approximations.

It can be shown by a mathematical analysis of the problem that it is possible to secure as many independent equations expressing functional relationship between the unknowns as there are unknown quantities, and therefore it is possible (at least in mathematical theory) to solve these equations simultaneously and secure numerical values for all of the unknowns. This method of solution in actual practice, however, proved so complex that we soon abandoned it in favor of the method of successive approximations, which, although tedious, is logically sound and gives the same result as a rigid mathematical solution, if carried out with sufficient patience.

We first obtained an approximate value for the hydrolysis constant,

$$K_H = \frac{(H)\ (Br)\ (HBrO)}{Br_2} = \frac{(H)^2 Br}{Br_2},$$

from the data of Table I. As a first approximation, we temporarily neglected the amount of tribromide and pentabromide formed, and computed from the conductivity the concentration of the H^+, Br^-, and HBrO, which was then subtracted from the total bromine giving the bromine present as Br_2, and we then computed K_H. A series of results obtained in this way showed a systematic variation as we pass from saturated to dilute solutions, owing to the neglect of tribromide and pentabromide, but nevertheless permitted the selection of an approximate value for K_H. The first approximation for K_H was 5.1×10^{-10}. The solutions saturated with bromine also gave as a first approximation for the concentration of Br_2, which is in equilibrium with liquid bromine, the value $Br_2 = 0.2497$.

The next step was to compute a first approximation for the distribution ratio of bromine (Br_2) between water and carbon tetrachloride. By neglecting temporarily the formation of tribromide and pentabromide, and computing the hydrolysis approximately by the aid of the hydrolysis constant already secured, we computed the Br_2 in the water layer, and hence obtained a first approximation for the ratio of the concentration of Br_2 in the

water and carbon tetrachloride. This distribution coefficient was found to be a linear function of the concentration in the carbon tetrachloride.

$$\frac{(Br_2 \text{ in } CCl_4)}{(Br_2 \text{ in } H_2O)} = 21.2 + 2.73\ (Br_2 \text{ in } CCl_4)$$

We then computed a first approximation for the equilibrium constant of the tribromide reaction from the data on the solutions which were not saturated with bromine. Approximate values for the Br_2 concentration were computed from the concentration of bromine in the CCl_4 layer, by the aid of our first approximation for the distribution ratio, and for the hydrolysis from our first approximation for the hydrolysis constant. Neglecting temporarily the formation of the pentabromide, we computed an approximate value for the tribromide concentration and hence secured a first approximation for the constant K_3. The results of such a calculation show a decided systematic variation within the series comparable with the similar variations found by Jakowkin[21] and Worley.[21] The value $K_3 = 0.057$ was selected as the first approximation.

It now remained to compute a first approximation for the equilibrium constant of the pentabromide reaction from the data on potassium bromide solutions saturated with bromine. By applying corrections for the presence of Br_2 from the data on the solubility of Br_2 in water, and for hydrolysis and the presence of tribromide by the aid of the first approximation for these constants, we obtained an approximate value for the pentabromide and hence for the equilibrium constant $K_5 = \frac{(Br^-)(Br_2)^2}{(Br_5)}$

The values for this constant showed a very large systematic variation within the series, since even in saturated solutions the amount of tribromide exceeds the pentabromide, and therefore error in the first approximation for K_3 has a large influence on K_5. The first approximation for K_5 was 0.017.

An attempt to secure approximate values for the mobility of the tribromide and pentabromide ion was made, but failed entirely at this stage, because of the very large systematic variation.

[21] *Loc. cit.*

In order to secure more accurate values for the various constants, we went back to the beginning again and computed a second approximation for the hydrolysis constant, but this time instead of ignoring the presence of tribromide and pentabromide, we made corrections for their presence by the use of the first approximations just secured. Here we assumed the mobility of the tribromide ion to be 30 and of the pentabromide ion to be 20. This gave the second approximation for K_H and Br_2 in a saturated solution. Then, in turn, second approximations for the distribution ratio, for K_3 and for K_5 were obtained. Here we found that the systematic variations of the constants with changes of concentration of KBr or bromine within a series were smaller than before, but still not eliminated entirely, and, moreover, the second approximations were different from the first approximations. This showed that the calculations must be repeated. This process was then continued until the systematic variations disappeared, and the successive approximations did not change by significant amounts.

In the following pages the mathematical procedure of these calculations is explained and tables are presented summarizing the final results.

In the following equations the concentrations of the various substances present are indicated by the chemical formulas, *e. g.*, H, K, Br, Br_2, Br_3, Br_5, HBrO, it being understood that Br_2 is free, whereas Br, Br_3, Br_5 are components of the potassium salts or the corresponding acids, including both the ionized and unionized portion. Λ_H, Λ_K, Λ_1, Λ_3, Λ_5, represent the mobilities of the ions H^+, K^+, Br^-, Br^-_3 and Br^-_5, respectively. The first three have the values 240, 40.1, and 43.7 at 0°. The values of Λ_3 and Λ_5 are to be deduced from the data.

κ is the specific conductivity of the solution under consideration.

R = moles free bromine (calculated as Br_2 or its equivalent) found by titration. Obviously $R = Br_2 + Br_3 + 2Br_5 + HBrO$.

C = moles Br_2 in carbon tetrachloride.

D = distribution ratio of Br_2 between carbon tetrachloride and water.

γ = degree of dissociation.

K_H, K_3, K_5 represent the equilibrium constants for the hydrolysis, the formation of tribromide, and of pentabromide, respectively, as defined by equations (12), (2), and (3) below.

A. The Calculation of the Hydrolysis Constant. When bromine is dissolved in water, the following reactions occur:

$$H_2O + Br_2 \leftrightharpoons H^+ + Br^- + HBrO.$$
$$Br^- + Br_2 \leftrightharpoons Br^-_3.$$
$$Br^- + 2Br_2 \leftrightharpoons Br^-_5.$$
Br_2 dissolved in water.

HBrO is completely undissociated, and the acids HBr, HBr_3, and HBr_5, are assumed to be completely ionized $\therefore$ $H^+ = HBrO$.

(1) $$1000\,\kappa = \wedge_H H + \wedge_1 Br + \wedge_3 Br_3 + \wedge_5 Br_5$$

(2) $$K_3 = \frac{Br.\ Br_2}{Br_3}$$

(3) $$K_5 = \frac{Br.\ Br_2{}^2}{Br_5}$$

(4) $$R = Br_2 + Br_3 + 2Br_5 + H$$

(5) $$H = Br + Br_3 + Br_5$$

$\wedge_H$, $\wedge_1$, $\wedge_3$, $\wedge_5$, K_3, and K_5 are known (only approximately in the first series, but more and more accurately with each succeeding repetition of the process of successive approximation). $1000\,\kappa$ and R are known (subject to unavoidable experimental error). That leaves five unknowns H, Br, Br_2, Br_3, Br_5, and since we have five equations, the numerical value of each can be found as follows,

(6) $$H = Br + \frac{Br.\ Br_2}{K_3} + \frac{Br.\ Br_2{}^2}{K_5}$$
from (2) (3) and (5)

(7) $$R = Br_2 + \frac{Br.\ Br_2}{K_3} + \frac{2Br.\ Br_2{}^2}{K_5} + H$$
from (2) (3) and (4)

$$(8) \qquad 1000\,\kappa = \wedge_H H + \wedge_1 Br + \wedge_3 \frac{Br.\ Br_2}{K_3} + \wedge_5 \frac{Br.\ Br_2^{\,2}}{K_5} \text{ from (1) (2) and (3)}$$

$$(9) \qquad (R - Br_2) = Br\left(1 + \frac{2Br_2}{K_3} + \frac{3Br_2^{\,2}}{K_5}\right) \text{ from (6) and (7)}$$

$$(10) \qquad 1000\,\kappa = Br\left(\wedge_H + \wedge_1 + (\wedge_H + \wedge_3)\frac{Br_2}{K_3} + (\wedge_H + \wedge_5)\frac{Br_2^{\,2}}{K_5}\right) \text{ from (6) and (8)}$$

$$(11) \qquad (R - Br_2)\left(\wedge_H + \wedge_1 + (\wedge_H + \wedge_3)\frac{Br_2}{K_3} + (\wedge_H + \wedge_5)\frac{Br_2^{\,2}}{K_5}\right) = 1000\,\kappa\left(1 + \frac{2Br_2}{K_3} + \frac{3Br_2^{\,2}}{K_5}\right) \text{ from (9) and (10)}$$

This can be reduced to the form

$$(11a) \qquad Br_2^{\,3} + ABr_2^{\,2} + BBr_2 + C = 0$$

$$\text{where } A = \frac{(\wedge_H + \wedge_3)\,K_5}{(\wedge_H + \wedge_5)\,K_3} - R + \frac{3000\,\kappa}{\wedge_H + \wedge_5}$$

$$B = \frac{K_5}{\wedge_H + \wedge_5}\left(\wedge_H + \wedge_1 - \frac{(\wedge_H + \wedge_3)\,R}{K_3} + \frac{2000\,\kappa}{K_3}\right)$$

$$C = \frac{K_5}{\wedge_H + \wedge_5}\,(1000\,\kappa - (\wedge_H + \wedge_1)\,R)$$

It is therefore possible to compute a numerical value for A and B and C and hence to solve equation (11a) by Horner's method, thus obtaining a numerical value for Br_2. Then in turn Br may be calculated from (9), Br_3 from (2), Br_5 from (3), and H from (5), and the whole checked by substitution in (4).

Then K_H can be computed from the definition

$$(12) \qquad K_H = \frac{(H)\ (Br)\ (HBrO)}{Br_2} = \frac{H^2(Br)}{Br_2}$$

The results of this computation for the last approximation are given in the table below.

TABLE VI.

Hydrolysis Constant.

R	$\kappa \times 10^6$	Br_2	$Br \times 10^3$	$Br_3 \times 10^3$	$Br_5 \times 10^3$	$H \times 10^3$	$K_H \times 10^{10}$
0.2563	286	0.253926	.126	.628	.331	1.085	5.84
0.1295	177	0.128228	.158	.398	.106	0.662	5.41
0.08919	144	0.088240	.176	.304	.0556	0.535	5.70
0.06940	124	0.068630	.181	.243	.0346	0.458	5.52
0.017817	67	0.017511	.177	.061	.0022	0.241	5.87
0.01242	57	0.012175	.164	.039	.0010	0.204	5.59
						Mean	5.7

The calculations in these tables are based on $K_3 = 0.0510$, $K_5 = 0.0246$, $\wedge = 240$, $\wedge_1 = 43.7$, $\wedge_3 = 23.5$, $\wedge_5 = 16.3$. An error of 1 per cent in the specific conductivity makes an error of 3 percent or 0.17 in K_H. The result obtained with the saturated solution is given extra weight in selecting the most probable value for K_H, since the data is the mean of several determinations. The values for K_H show no systematic variation and the variations are within the unavoidable experimental error. We therefore conclude that $K_H = 5.7 \times 10^{-10}$ at 0°, and that the concentration of Br_2 in a solution in equilibrium with liquid bromine is 0.2539. Bray and Connolly found that at 25° C. $K_H = 5.2 \times 10^{-9}$ and $Br_2 = 0.2068$.

B. The Calculation of the Distribution Ratio of Bromine (Br_2) Between Water and Carbon Tetrachloride. The dissolved bromine in both phases having been determined by titration, it is then necessary to calculate the amount present as HBrO, Br_3 and Br_5 in order to compute the amount present as Br_2.

Besides equations (2), (3), (4), (5), (6) and (12), we have the following:

$$(13) \qquad Br = \frac{H}{1 + \frac{Br_2}{K_3} + \frac{Br_2^{\,2}}{K_5}} \quad \text{from (6)}$$

$$(14) \qquad K_H = \frac{H^3}{Br_2\left(1 + \frac{Br_2}{K_3} + \frac{Br_2^{\,2}}{K_5}\right)} \quad \text{from (12) and (13)}$$

$$(15) \qquad H = \sqrt[3]{K_H Br_2\left(1 + \frac{Br_2}{K_3} + \frac{Br_2^{\,2}}{K_5}\right)} \quad \text{from (14)}$$

It is most convenient to proceed by applying the method of successive approximations. First assume $Br_2 = R$ and then compute H from (14), Br from (7), Br_3 from (3), and Br_5 from (2). Then from equation (4) compute a more accurate value for Br_2, which is then substituted in (14), giving a better value for H, and then in turn Br, Br_3, and Br_5 are computed, and then again Br_2 is found from (4). A third repetition of this process in no case changed the value of Br_2. The concentration of bromine in the carbon tetrachloride is then divided by the concentration of Br_2 in the water, giving the distribution ratio. This distribution ratio is a linear function of the concentration of bromine.

The results of this calculation are given in the table below.

The values of the other constants used in this calculation were, $K_3 = 0.0510$, $K_5 = 0.0246$, $K_H = 5.7 \times 10^{-10}$.

TABLE VII.

Summary of Results on Distribution.

C Br_2 in CCl_4	R	Br_2	D	D′	D-D′
1.8194	0.07015	0.06936	26.23	26.17	+0.06
0.9218	0.03937	0.03886	23.72	23.63	+0.09
0.8666	0.03771	0.03721	23.29	23.47	—0.18
0.7676	0.03344	0.03299	23.27	23.19	+0.08
0.6442	0.02870	0.02829	22.77	22.84	—0.07
0.5695	0.02572	0.02534	22.48	22.63	—0.15
0.1903	0.00901	0.00880	21.63	21.56	+0.07
0.1687	0.008007	0.00781	21.60	21.50	+0.10

When D was plotted against C, the curve formed was found to be a straight line. The equation of this line was calculated by the method of least squares to be

$$D = 21.018 + 2.831\ C.$$

The column D′ gives the results calculated from this equation.

C. Calculation of K_3 from data on solutions unsaturated with respect to bromine. Here we have the following equations:

(16) $$K + H = Br + Br_3 + Br_5$$

(4) $$R = Br_2 + Br_3 + 2Br_5 + H$$

(12) $$K_H = \frac{H^2Br}{Br_2}$$

(3) $$K_5 = \frac{Br\ Br_2{}^2}{Br_5}$$

(17) $$K - R + Br_2 = Br - Br_5 - 2H = Br\left(1 - \frac{Br_2{}^2}{K_5}\right) - 2H \text{ from (16) (4) and (3)}$$

(18) $$2H + (K - R + Br_2) = \frac{K_H Br_2}{H^2}\left(1 - \frac{Br_2{}^2}{K_5}\right) \text{ from (17) and (18)}$$

(19) $$H^3 + \frac{1}{2}(K - R + Br_2)H^2 - \frac{1}{2}K_H Br_2\left(1 - \frac{Br_2}{K_5}\right) = 0 \text{ from (18)}$$

Here everything is known except H. Solve for H by Horner's method. Then get Br from (17), Br_5 from (3), and Br_3 from (16), and check the result in (4).

Table VIII.

Unsaturated Solutions.

The calculations are based on $K_H = 5.7 \times 10^{10}$; $K_5 = 0.0246$; $D = 21.018 + 2.831\ C$.

K	R	C	$\kappa \times 10^6$	$Br_2 \times 10^3$	$H \times 10^3$	$Br \times 10^3$	$Br_5 \times 10^3$	$Br_3 \times 10^3$	K_3	γ	$\kappa \times 10^6$ calc.	κ calc.–κ obs.
0.10054	0.08070	0.8278	6603	35.43	0.019	58.29	2.97	39.30	0.0526	0.873	6595	—8
0.04919	0.06209	0.9124	3290	38.66	0.028	27.49	1.67	20.06	0.0530	0.897	3300	+10
0.04931	0.03239	0.4083	3483	18.42	0.017	35.37	0.49	12.96	0.0510	0.897	3497	+14
0.01989	0.01735	0.2854	1475	13.06	0.022	15.77	0.11	4.03	0.0511	0.926	1471	—4
0.01988	0.01851	0.3053	1441	13.95	0.023	15.49	0.12	4.29	0.0504	0.926	1465	+24
0.009995	0.01533	0.2887	757	13.222	0.031	8.005	0.057	1.964	0.0539	0.947	763	+6
0.009995	0.013595	0.2519	765	11.592	0.028	8.093	0.044	1.886	0.0497	0.947	770	+5
0.004997	0.015304	0.3064	396	14.000	0.046	3.817	0.030	1.195	0.0447	0.958	390	—6
0.004996	0.019652	0.4030	393	18.187	0.053	3.686	0.040	1.313	0.0510	0.958	389	—4
0.001963	0.019604	0.4185	180	18.847	0.088	1.401	0.020	0.623	0.0420	0.980	172	—8
									0.051			

The values for Λ_3 and Λ_5 were found by computing the specific conductivity, assuming $\Lambda_H = 240$, $\Lambda_K = 40.1$, $\Lambda Br = 43.7$, and also assuming that the degree of ionization of each of the salts KBr, KBr_3, and KBr_5 in the mixture is the same as that of the original potassium bromide solution before adding bromine. The results in the next to the last column were computed with $\Lambda_3 = 23.5$ and $\Lambda_5 = 16.3$.

The values for K_3 no longer show any systematic variation. They are somewhat variable, it is true, but the experimental errors are much magnified during the calculations, especially in the more dilute solutions; for example, in the case of the 0.002 solution an error of 0.1 percent in the titration will make an error of 5 percent in K_3.

D. Calculation of K_5 from data on solutions saturated with bromine. K_3, K_H, and the concentration of Br_2 are known. Numerical values of K and R for each solution are obtained experimentally.

(16) $$K + H = Br + Br_3 + Br_5$$

(4) $$R = Br_2 + Br_5 + 2Br_5 + H$$

(2) $$K_3 = \frac{Br\ Br_2}{Br_3}$$

(12) $$K_H = \frac{H^2Br}{Br_2}$$

(22) $$3H + 2K - R + Br_2 = 2Br + Br_3$$
from (16) and (4)

(23) $$3H + 2K - R + Br_2 = Br\left(2 + \frac{Br_2}{K_3}\right)$$
from (22) and (2)

$$H^3 + \frac{1}{3}(2K - R + Br_2)\,H^2 - \frac{1}{3}K_HBr_2\left(2 + \frac{Br_2}{K_3}\right) = 0$$ from (23) and (12)

Here everything is known except H. Solve for H by Horner's method, then get Br from (23), Br_3 from (2) and Br_5 from (16), and check the calculation by (4). Then compute

$$K_5 = \frac{Br\ Br_2{}^2}{Br_5}.$$

Table IX.

Solutions Saturated with Bromine.

K	R	$\kappa \times 10^6$	$H \times 10^3$	$Br \times 10^3$	$Br_3 \times 10^3$	$Br_5 \times 10^3$	K_5	γ	$\kappa \times 10^6$ Calc.	κ Calc — κ Obs.
0.09819	0.3796	5491	0.114	11.04	54.96	32.30	0.0220	0.873	5470	— 21
0.09906	0.3734	5520	0.113	11.32	56.34	31.51	0.0232	0.873	5528	+ 8
0.05102	0.3149	2943	0.156	5.95	29.63	15.60	0.0246	0.897	2954	+ 11
0.04947	0.3127	2853	0.158	5.82	28.99	14.82	0.0253	0.897	2868	+ 15
0.019815	0.2776	1228	0.246	2.39	11.91	5.76	0.0267	0.926	1233	+ 5
0.019766	0.2779	1272	0.248	2.38	11.63	6.05	0.0248	0.926	1228	— 44
0.009905	0.2667	680	0.353	1.16	5.77	3.33	0.0224	0.944	683	+ 3
0.009449	0.2661	665	0.368	1.13	5.63	3.10	0.0235	0.945	660	— 5
0.008899	0.2656	....	0.373	1.04	5.16	3.07	0.0218	0.947	....	
0.004941	0.2605	431	0.464	.673	3.35	1.38	0.0313	0.957	421	— 10
0.002842	0.2586	330	0.600	.402	2.00	1.04	0.0249	0.965	328	— 2
0.001976	0.2577	299	0.677	.316	1.57	.766	0.0266	0.969	296	— 3
0.000988	0.2570	278	0.842	.204	1.02	.611	0.0215	0.973	279	— 1
						mean	0.0246			

The calculations recorded in this table are based on $K_H = 5.7 \times 10^{-10}$, $K_3 = 0.0510$, and $Br_2 = 0.25392$. The specific conductivity has been computed with $\Lambda_H = 240$, $\Lambda_K = 40.1$, $\Lambda_1 = 43.7$, $\Lambda_3 = 23.5$, and $\Lambda_5 = 16.3$. The values for K_5 show no systematic variation. The values for K_5 are very sensitive to errors in the experimental data and in the values accepted for K_3 and K_H, especially in the dilute solutions. With the 0.01n solution an error of 0.1 percent in R makes an error of 10 percent in K_5, and with the 0.001n solution an error or 0.1 percent in R makes an error of 25 percent in K_5. It should be noted that in these saturated solutions the Br is only about one-fifth of the Br_3 and one-third of the Br_5.

Summary.

Measurements of the equilibrium between bromine and water and bromine and potassium bromide solutions at 0°, and of the specific conductivity of the solutions have been made. Computations based upon the results show that the following reactions occur, and that a quantitative interpretation may be secured without the necessity of assuming that any other reactions occur:

1. Bromine dissolves as Br_2.
2. $Br_2 + H_2O \leftrightarrows H^+ + Br^- + HBrO$.
3. $KBr + Br_2 \leftrightarrows KBr_3$.
4. $KBr + 2Br_2 \leftrightarrows KBr_5$.

A saturated solution of bromine in water at 0° has the composition: Br_2, 0.2539 moles per liter; H^+, 0.001085; Br, 0.000126; Br_3, 0.000628; Br_5, 0.000331.

$$\text{The hydrolysis constant, } K_H = \frac{(H)(Br)HBrO}{Br_2} = 5.7 \times 10^{-10}.$$

$$\text{The equilibrium constant, } K_3 = \frac{Br^- \times Br_2}{Br^-_3} = 0.051.$$

$$\text{The equilibrium constant } K_5, = \frac{Br^- \times Br_2^2}{Br^-_5} = 0.0246.$$

The distribution coefficient of Br_2 between water and carbon tetrachloride (after correcting for hydrolysis) is, $D = 21.018 + 2.831\ C$, where C is concentration of Br_2 in the carbon tetrachloride.

By the aid of these constants the concentration of each ion may be computed in any solution containing known amounts of potassium bromide up to 0.1n, and known amounts of bromine up to saturation.

The conductivity of a series of potassium bromide solutions from 0.001n to 0.1n has been determined at 0° C. These results when extrapolated to infinite dilution by the method of A. A. Noyes give 83.8 for the mobility of potassium bromide, and if the value for the mobility of the potassium ion is 40.1, the mobility of the bromide ion is 43.7. From the data for the specific conductivity of solutions containing bromine we conclude that the mobility of the tribromide ion is 23.5, and of the pentabromide ion, 16.3.

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Harvard University, Cambridge, Mass.

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A NEW METHOD FOR THE STUDY OF SILVER PEROXYNITRATE.

By Mortimer J. Brown.

When an aqueous solution of silver nitrate is electrolyzed between insoluble electrodes under certain conditions, a black compound of silver is formed at the anode. This compound was first described by Ritter in 1804, and many people since then have tried to establish its composition. Margrete Bose[1] and Baborovsky and Kuzma[2] have given literature references to the more important papers which are here repeated with one or two additions.[3] Some of the formulas which have been suggested for this silver salt are as follows:

Ag_2O_2—Wallquist.
$Ag_2O.Ag_2O_3$—Brauner and Kuzma (1907).
Ag_2O_3—Luther and Pokorny (1908).
Ag_3O_4—Baborovsky and Kuzma (1909).
$Ag_4O_5.AgNO_3$—Fischer.
$2Ag_2O_2.AgNO_3.H_2O$—Fischer.
$5Ag_2O_2.2AgNO_3.H_2O$—Mahla.
$4Ag_2O_3.2AgNO_3.H_2O$—Berthelot (1881).
$Ag_2O_3.2AgNO_3$—Hampe (1890).
$3Ag_2O_2.O_2.AgNO_3$—Mulder and Heringa (1896).
$2Ag_3O_4.AgNO_3$—Tanatar (1901).
$3Ag_4O_5.2AgNO_3$—Sulc (1896).
$3Ag_2O_2.O_2.AgNO_3$—Sulc (1900).

[1] Zeit. anorg. Chem., **44**, 262 (1907); *Cf.* also Gmelin Kraut's Handbuch der anorg. Chem., **5**, II, 69 (1908).

[2] Zeit. phys. Chem., **67**, 48 (1909).

[3] Ritter: Gehlens neues Jour., **3**, 561 (1804); Wallquist: Jour. prakt. Chem., **31**, 179 (1842); Fischer: *Ibid.*, **33**, 237 (1844); Grotthuss: Jahresber. Chem., **1852**, 423; Mahla: Liebig's Ann., **82**, 289 (1852); Berthelot: Comptes rendus, **90**, 653 (1880); Hampe: Chem. Zeitung, **14**, 1777 (1890); Novák: Rozpravy Ceské Akad., **5**, No. 6 (1896); Sulc. Zeit. anorg. Chem., **12**, 89, 180 (1896); Mulder and Heringer: Rec. Trav. chim. Pays. Bas., **15**, 1, 236 (1896); Mulder: *Ibid.*, **16**, 57 (1897); **17**, 57 (1898); **18**, 91 (1899); **19**, 115, 165 (1900); **32**, 385; **21**, 405 (1903); Sulc: Zeit. anorg. Chem., **24**, 305 (1900); Tanatar: *Ibid.*, **28**, 331 (1901); Kuzma: Rozpravy Ceské Akad., **19**, No. 11 (1905); Watson: Jour. Chem. Soc., **89**, 578 (1906); M. Bose: Zeit. anorg. Chem., **44**, 237 (1907); Wilkinson and Gillett: Jour. Phys. Chem., **11**, 382 (1907); Brauner and Kuzma: Ber. deutsch. chem. Ges., **40**, 3371 (1907); Luther and Pokorny: Zeit. anorg. Chem., **57**, 290 (1908); Baborovsky and Kuzma: Zeit. phys. Chem., **67**, 48 (1909); M. Bose: *Ibid.*, **68**, 383 (1909); Barbieri: Gazz. chim. ital., **42**, II, 7 (1912).

Margrete Bose[4] determined the decomposition point for silver nitrate solution and silver sulphate solution. Only one break was found in each solution and consequently she concludes that only one compound is formed at the anode in each case. A platinum wire anode was used and the other pole was a N/10KCl calomel electrode, the potential difference of which was called 0.33 volts against the hydrogen electrode taken as zero. The anode decomposition voltage for silver nitrate solution was found to be 1.573 volts and that for silver sulphate solution 1.53 volts. Although the decomposition voltage is higher in the more concentrated nitrate solution, the author considers that these two values are the same and that the difference is due to a difference in potential between the two solutions. On that basis the conclusion is drawn that the precipitate is the same from the two solutions and consequently cannot contain either silver nitrate or silver sulphate.[5]

"The precipitated silver oxide is unquestionably the same in the two cases. Regardless of the solution the oxide precipitates in exactly the same form as beautiful, sepia-colored crystals with metallic lustre. There seems no reason for assuming that we are dealing with two different substances, such as compounds of a silver oxide with silver nitrate or silver sulphate. When one remembers how many chemically prepared compounds can only be washed free from adhering mother liquor with great difficulty, and how often crystals contain enclosed mother liquor, it is not surprising that these crystals, formed by electrolysis and precipitated very rapidly, should contain some of the solution in which they grew."

The difference between 1.573 volts and 1.53 volts is nothing like as large as the changes in the decomposition voltage of silver nitrate solutions with varying concentration and varying amounts of nitric acid,[6] which may be taken as an argument in favor of or against the assumption that the same compound is precipitated from silver nitrate and silver sulphate solutions. Margrete Bose[7] made no analyses because she considered it impossible to get accurate results.

[4] Zeit. anorg. Chem., **44**, 237 (1907).
[5] M. Bose: Zeit. anorg. Chem., **44**, 263 (1907).
[6] Wilkinson and Gillett: Jour. Phys. Chem., **11**, 382 (1907).
[7] Zeit. phys. Chem., **68**, 383 (1909).

Luther and Pokorny[8] determined the voltage-current curve for a silver anode in caustic soda solution. They obtained one break corresponding to Ag_2O and one corresponding to Ag_2O_2. Silver is oxidized quantitatively to silver oxide and then quantitatively to silver peroxide. The peroxide is reduced quantitatively to oxide and then to metal. The following equilibrium potentials were observed.

$$Pt(H_2) \mid N.NaOH \mid N.NaOH,Ag_2O \mid Ag = 1.170 \text{ V.}$$
$$Pt(H_2) \mid N.NaOH \mid N.NaOH,Ag_2O_2,Ag_2O \mid Pt = 1.40 \text{ V.}$$

from which follows[9]

$$Pt(H_2) \mid N.NaOH \mid N.NaOH,Ag_2O_2 \mid Ag = 1.285 \text{ V.}$$
$$Ag \mid Ag_2O,N.NaOH \mid N.NaOH,Ag_2O,Ag_2O_2 \mid Pt = 0.23 \text{ V.}$$

It was shown that these values were practically independent of the concentration of the hydroxyl ions, as required by theory.

Luther and Pokorny then prepared Mulder's so-called peroxynitrates and peroxysulphates, washed them repeatedly with water and caustic soda[10] and reduced them at constant current in normal caustic soda. Three definite potentials were observed against hydrogen in normal caustic soda, one at 1.57 volts, a second at 1.41 volts, and a third at 1.17 volts. The second and third evidently correspond to the Ag_2O_2, Ag_2O and Ag_2O, Ag stages respectively. The value of 1.57 volts must correspond to a higher oxide, to which Luther and Pokorny assign tentatively the formula, Ag_2O_3. Since the same curves were obtained with Mulder's so-called peroxynitrate and peroxysulphate, the authors conclude as M. Bose had done, that neither silver sulphate nor silver nitrate is an integral part of the compound, which is therefore an impure oxide of silver.

In flat contradiction with this are the conclusions of Sulc[11] and of Watson.[12] Sulc says: "I believe that I have shown that the crystalline substance formed at the anode, when aqueous silver nitrate solutions are electrolyzed between platinum electrodes, has a composition corresponding to the formula Ag_7NO_{11} and that it loses five atoms of oxygen gradually when heated, leaving

[8] Zeit. anorg. Chem., **57**, 290 (1908).
[9] Calculated according to Luther and Wilson: Zeit. phys. Chem., **34**, 488 (1900).
[10] [This would decompose them to some extent. M. J. B.]
[11] Zeit. anorg. Chem., **24**, 312 (1900).
[12] Jour. Chem. Soc., **89**, 578 (1906).

behind a complex Ag_7NO_6 which is to be considered as $3Ag_2O.AgNO_3$. Three out of the five atoms of oxygen are to be considered as different from the other two, because only these three take part in the reaction with ammonia and probably with oxalic acid (unfinished experiments). It is probably these three atoms of oxygen which give the substance the properties of a peroxide, as shown in its energetic oxidizing action.[13] These properties can be represented provisionally by the formula $AgNO_3.3Ag_2O_2.20$."

Marshall[14] says: "I have varied the conditions of electrolysis of silver nitrate by altering the current-concentration and density and also the strength of solution, and have found the product to be the same in all cases and identical with the compound described by Sulc. This disposes of the possibility of this definitely crystallized product being a mixture. Sulc has satisfactorily investigated the effect of heat on this peroxynitrate. I have not been able to confirm Sulc's analytical data for the reaction of the peroxynitrate with ammonia.

"I have examined the decomposition of the peroxynitrate by water. Even at the ordinary temperature of the laboratory (27°-32°), reaction occurs slowly with the evolution of oxygen. This change occurs more readily on boiling, and is complete in less than an hour. Oxygen is evolved, part of the silver goes into solution, and there remains a black substance which I have found to be silver dioxide, Ag_2O_2, probably obtained pure for the first time. The course of the reaction is represented by the equation:

$$Ag_7NO_{11} = AgNO_3 + 3Ag_2O_2 + O_2.$$

"I have determined quantitatively the correctness of this expression for the decomposition of the peroxynitrate by boiling, and also the composition of the insoluble substance as being that of silver dioxide. It is a greyish-black powder of sp. gr. 7.44, approximately, which may be heated to 100° without change. At a higher temperature, it evolves oxygen and leaves a residue of silver.

[13] The "silver peroxide" inflames dry hydrogen gas at ordinary temperature just as other metallic peroxides do, lead peroxide (Vanino and Hausner: Ber. deutsch. chem. Ges., **33**, 625 (1900)) or thallium peroxide (Carstanjen: Jour. prakt. Chem., **102**, 77 (1867)) for instance.

[14] Jour. Chem. Soc., **89**, 579 (1906).

"The behavior of the dioxide with ammonia is remarkable; it dissolves with the evolution of nitrogen, but in the amount required by the equation:

$$6Ag_2O_2 + 2NH_3 = N_2 + 3H_2O + 3Ag_4O_3,$$

and not, as would have been expected, in accordance with the equation:

$$3Ag_2O_2 + 2NH_3 = N_2 + 3H_2O + 3Ag_2O.$$

"Both the peroxynitrate and the dioxide of silver, also the peroxysulphate produced by the electrolysis of aqueous silver sulphate solution, dissolve in cold strong nitric acid with the production of an intensely brown solution, and in cold strong sulphuric acid with an olive-green color. These colors are due to the formation of silver peroxy-salts. It can hardly be doubted that the same colored salt is formed from the peroxynitrate as from the dioxide, because the colors and absorption spectra of the solutions obtained from the three substances are identical. These colored salts gradually decompose at the ordinary temperature, and more quickly on heating or on adding water, silver sulphate or nitrate remaining in solution. Up to the present, attempts to isolate these peroxy-salts have been unsuccessful. During the decomposition of these solutions, some evolution occurs of what appears to be oxygen, but no hydrogen peroxide is formed."

Working in pyridine solution Barbieri[15] has prepared silver persulphate with pyridine of crystallization, $Ag_2S_2O_8.,4Pyr$; but this really has no bearing on our problem because Luther and Pokorny have proved that silver peroxide, Ag_2O_2, can exist and that it is not identical with the so-called peroxynitrate.

Since the composition of the so-called silver peroxynitrate has not been determined with a satisfactory degree of accuracy, it seemed desirable to make another attempt to get a satisfactory analysis of the compound. This investigation was undertaken at Prof. Bancroft's suggestion and was carried out under his direction. The experimental work was suddenly and reluctantly abandoned in 1911 and is published at this time because there is no hope that the author will be able to take it up again.

[15] Gazz. chim. ital., 42, II, 7 (1912).

When silver nitrate solution is electrolyzed between insoluble electrodes, silver is deposited at the cathode and silver peroxynitrate at the anode, there being presumably a simultaneous formation of nitric acid at the anode. Both solid deposits are crystalline, and they grow rapidly one toward the other in arborescent crystals. Because of this fact, there is no doubt that the anode product is a good electrical conductor. However, almost as soon as the electrolysis begins, the black crystals break away from the anode, are attacked by the nitric acid in solution and eventually go entirely into solution with liberation of gas.

After studying this electrolysis carefully and at considerable length in a variety of types of apparatus, transparent and opaque, the author became strongly of the opinion that so long as the peroxynitrate remained in electrical contact with the anode it was not attacked by the nitric acid simultaneously formed. It therefore seemed possible to develop a type of apparatus which would permit of the quantitative electrolytic precipitation of the peroxynitrate and the checking of its weight against the gain in copper coulometers in the same electric circuit. Previous investigators had used no apparatus specially adapted to the problem in hand, and it is highly probable that none of them had for purposes of analysis more than a part of the material originally deposited, much of it having been lost by being dissolved in the electrolyte. This one supposition held the possible explanation for discrepancies between the analyses and conclusions of different men. Special apparatus was therefore developed.

THE APPARATUS.

In Fig. 1, *A* is a capsule of glass. The edges at the top are well fired so that the one hole rubber stopper can be inserted tightly and smoothly with no cutting of the rubber. The shoulder is square as shown, and the small glass tube constituting the lower part of the capsule is also well rounded on its edges so that it can be easily inserted into the tightly fitting rubber tube which serves, with the rubber stopper mentioned above, to connect the capsule into the apparatus. The capsule measures 3.8 cm. x 2.3 cm. over all and above the shoulder it measures 2 cm. x 1.6 cm.

inside. Upon the shoulder rests the filter and anode which will be described later.

B is a composite piece, of glass. The cathode chamber b_1 is closed by the stopcock 11 at the bottom, and by a one-hole rubber stopper at the top. The chamber b_2 serves to maintain a good head of electrolyte and also to hold a filter on the square shoulder as shown. This filter consists of a layer of hardened filter paper between two perforated porcelain plates.

C serves, first, as a holder for the cathode; second, as an exit for air when the apparatus is being filled with solution; third, as an inlet for air and also for wash water when the solution is being removed from the apparatus. The cathode c_1 is a silver

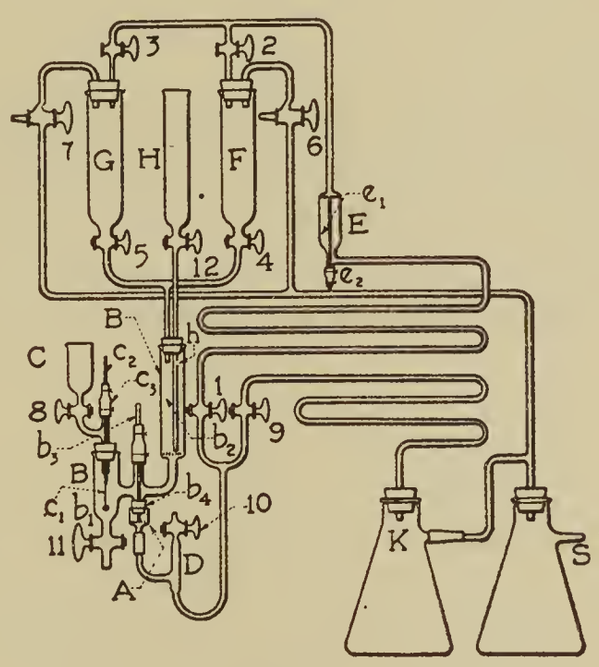

FIG. 1.

wire sealed into the small glass tube c_2 which is in turn filled with mercury in the well known manner. The rubber tube c_3 provides an air-tight yet non-rigid connector between c_2 and the larger tube around it.

Electrical contact with the anode in capsule *A* is provided by means of the small glass tube b_3 which has a very fine platinum point sealed through its end, and is also filled with mercury. The tube is very small throughout most of its length, so that the cross section of the column of electrolyte from anode to cathode may be as large as possible, to provide good conductivity. The upper end of this tube is made large so that a good surface may be

presented to the rubber tube around it. When setting up the apparatus, this rubber tube is wired into position in such a manner that a slight tension holds the platinum point firmly on the anode, thus securing a good electrical contact.

E is a container for suspended silver carbonate. There is a square shoulder at the upper end, against which a filter is held, the filter consisting of one layer of hardened filter paper between two perforated porcelain plates. This filter is held in position by means of the small glass rod e_1 which is held firmly by the tension of rubber tube e_2.

H is a special form of tube extending down into *B*. The lower end rests firmly against the filter, holding the latter in place. There is a small opening in one side of the tube h_1, well below the rubber stopper.

With the exception of the seven rubber stoppers and three pieces of rubber tubing represented in the drawing, the containing apparatus is entirely of glass, hardened filter paper, porcelain, platinum and gold.

The function of other parts of the apparatus will be apparent from what follows.

MANIPULATION.

Let it be assumed that the apparatus is clean and ready for use. An unweighed capsule *A* is fitted into place. All stopcocks but 12 are closed. Suction is applied to the system at *S*. Silver nitrate solution is poured into *H*. Stopcock 6 (or 7) and 2 (or 3) are opened, followed by a cautious opening of 1. Solution passes through *B, A, D,* and *E* into *F* with a speed dependent upon the manipulation of 1. Before all of the electrolyte is introduced, *A* is replaced by a funnel through which suspended silver carbonate can be introduced into the system. This carbonate is not able to pass *E*. *A* is replaced; the addition of electrolyte proceeds until *F* or *G* is full, and also both compartments of *B*. It will be noticed that the details of construction prevent the solution from touching either of the two rubber stoppers in the compartments of *B*. Compartment *G,* being empty, continuous circulation of electrolyte is begun and maintained as follows: (Stopcock 1 is always used for final control) Close 2; connect *F* to air

by means of 6; open 4; (electrolyte rises to same height in *H* as in *F*) connect *G* to *S* by 7; open 3; cautiously open 1. Electrolyte passes from *F* and *H* into *B* which remains full up to h_1; thence through *A*. *D*. *E* and into *G*. As soon as *F* is empty, close 4; connect *F* to *S* by 6; open 2; close 3; connect *G* to air by 7; open 5; as soon as *G* becomes empty, the cycle is completed, regular repetition of which gives continuous circulation. As soon as the apparatus is working smoothly and the electrolyte is clear of silver carbonate (excepting of course in *E*), quantitative electrolysis is begun by emptying *B* and *A* and exchanging for the latter a new, weighed capsule and filler. After electrical connections are made ready circulation is started, after which the circuit is closed.

After the electrolysis has proceeded far enough, 4 and 5 are closed; the solution level is allowed to run down toward the lower end of b_2; distilled water is then quickly poured into *H* and *C*; 8 is opened; 9 is opened and 1 immediately closed; distilled water is added to *H* and *C* until the milliammeter shows that no more current is passing, whereupon the capsule is sucked dry and removed from the apparatus.

This manipulation requires practice, but great skill is not required for successful operation. The complexity of the apparatus is a result of the satisfaction of several very exacting needs:

1. A continuous, well controlled circulation can be maintained as explained above.

2. The nitric acid formed at the anode is removed immediately from the zone of formation and is continuously and very thoroughly neutralized by reaction with suspended silver carbonate. On any ordinary filter, silver carbonate packs so badly that a solution can not be pulled with any practicable speed through it. In this apparatus a relatively large amount of silver carbonate can be used in *E*, without the inconvenience of a packed filter. Practically none of the carbonate escapes this filter, and what does is caught on the filter in *B*. The gas which is formed by the neutralization of the nitric acid escapes from the system by way of *S*.

3. In such work as this it is desirable and almost essential that the solutions be limited in volume. This apparatus used about 100 cc. of solution.

4. The construction of the apparatus ensures freedom from contamination. The materials used are glass, hardened filter paper, porcelain, platinum, gold and rubber. Rubber touches the solution only at *A* and *E*, and it is seemingly not acted upon during the course of many electrolyses.

5. At times the solution becomes heated during electrolysis. By bringing a large beaker of ice water up around *A* and *B*, satisfactory refrigeration can be maintained.

SPECIFIC DETAILS OF CONSTRUCTION AND MANIPULATION.

The capsule *A* is made with a square shoulder to give stability to the anode and filter. The combination is made as small as possible so that the total weight is such as to permit of analytical accuracy. In the early experiments made by the author, asbestos filters were tried and abandoned; the lack of success attending their use was due to the fugitive character of fine asbestos fibers in such a circulating solution. However, after perfecting the apparatus and acquiring skill at manipulation, asbestos filters were used with surprising success in the experiments 28 and 29. Unfortunately, alundum or similar porous plates were not tried. Paper filters were used for experiments 1 to 27 inclusive. There were used, in order from top to bottom, a perforated platinum plate, a perforated porcelain plate under and around the edges of which were a sufficient number of hardened filters (generally three) to make a tight fit. All but one of these hardened papers were used with their centers cut out, so that too great an obstruction was not offered to the moving liquid. For experiments 28 and 29, the capsules were made up so that there were in order from top to bottom, a gold plated perforated platinum plate, an asbestos filter, a perforated porcelain plate and three hardened paper filters, two of which had their centers removed. While asbestos filters can be made to work well, their use is not advisable because of the desirability of using the same capsule and filter repeatedly, a constant weight of which greatly enhances the reliability of data obtained. Were the author ever to resume this investigation he would endeavor to have the apparatus specially constructed to take accurately fitting porous plates which would render unnecessary the use of paper.

The cathode c_1 is a platinum or silver wire of small surface, so that the silver crystals can be broken off by a gentle tapping of the glass tube c_2. This is very important, for the silver crystals grow with such surprising rapidity that a tongue of silver can easily bridge the gap between the cathode and the horizontal tube leading to *A*. If this once happens during an electrolysis, the crystal grows within a very few seconds of time over into the region above *A* and drops minute crystals of silver upon the anode deposit. These thin crystals are sometimes detected with great difficulty even in good light, and since a horizontal layer of silver, though detached from the cathode, acts bipolar with the resultant production of such crystals, great care must always be taken. In the earlier forms of this apparatus, data from which are not reported in this paper, the cathode was placed above the filter in *B*. Such construction was abandoned because silver always grew through the filter. During electrolysis it is necessary to tap the tube c_2 occasionally in order to break off the long needle crystals from the cathode. They settle quickly to the bottom of b_1.

The tubes from *D* to *E* and *K* must be of the zigzag form commonly used in glass apparatus of this type; the capsules can be changed freely, with no danger of breakage.

D is a gas trap. At the beginning of an electrolysis it is entirely filled with solution. If at any time an appreciable amount of gas is formed at the anode and is drawn through the filter, it is caught in *D*. Although gas did form during these experiments as will be recorded below, at no time was there enough to make a small-sized bubble in *D*, in other words this gas trap only served to demonstrate that no measurable amount of gas was being drawn through the filter in such a manner as to escape detection.

Two copper coulometers were used in all work, the one serving as a check upon the other. The solution was as follows: 150 g. copper sulphate, 50 g. sulphuric acid, 50 g. alcohol and one liter of distilled water. Two anodes were used in each coulometer. The cathodes were of copper foil to give lightness of weight, and each cathode below the solution measured 2.5 cm. x 10 cm. on each face. They never weighed more than 5 g. each.

The silver nitrate used was obtained by recrystallizing the C. P. salt found in the laboratory stock. The solutions were carefully preserved and were never used if any turbidity was apparent.

METHODS OF WASHING, WEIGHING AND ANALYZING THE PEROXYNITRATE.

It was presumed from the beginning of the investigation that the peroxynitrate was more or less unstable, and that therefore the methods of washing and weighing were of fundamental importance. It was found that capsules made up with complete filters could be washed freely with water, silver nitrate solution, dilute nitric acid, ammonium hydroxide and alcohol with losses so small that errors of weighing generally masked any losses of weight. The reason for using ammonium hydroxide was that it dissolves peroxynitrate; but since a good white filter could not be thus obtained, dilute nitric acid was always used as a supplementary cleansing agent. Water was used to remove all soluble materials, and absolute alcohol to remove water, which because of the slowness of evaporation tended to decompose the peroxynitrate on a wet filter.

Washing and drying operations were not standardized until after the tenth experiment. Beginning with the eleventh experiment, the capsules with fresh precipitate were washed quickly with distilled water until all silver nitrate was removed, then with absolute alcohol to remove water, after which air (dried with conc. H_2SO_4) was forced through the capsules for a few minutes until the alcohol was all removed. After weighing, this treatment could be repeated with no appreciable loss of weight; hence the conclusion that alcohol did not react upon the peroxynitrate. The use of alcohol was considered to be warranted by reason of the rapid desiccation thus secured. The undesirable effect of slow drying was demonstrated by the following tests:

A fresh lot of peroxynitrate was made and divided into three parts. The first sample was left on the filter in the capsule and washed with successive 10 cc. portions of distilled water. These portions of wash water were examined for silver by adding HCl. Before making the tests the product was hurriedly washed to remove the last traces of silver nitrate. The first five tests were made within fifteen minutes after the above mentioned washing. Thirty minutes elapsed between the fifth and sixth washings, one hour between the sixth and seventh, and fifteen minutes between the seventh and eighth. The addition of HCl resulted as follows:

1. Very perceptibly turbid. 2. Slightly turbid. 3. Very slightly turbid. 4. Presence of silver questionable. 5. Very slightly turbid. 6. Slightly more than in 5. 7. Turbid. 8. More silver than in any other except 1. Hence the conclusion that the peroxynitrate decomposes to an appreciable extent in water at ordinary temperature and pressure.

The second part of the peroxynitrate was placed in a small weighing bottle in previously boiled and cooled distilled water. It was then placed under low pressure in a vacuum desiccator. Within five minutes from the time the pressure was reduced, there was an easily observable evolution of gas from the peroxynitrate, and it continued for several hours.

The third part of the peroxynitrate, in a capsule, was connected between a Hempel mercury gas burette and a Hempel mercury gas pipette, both miniature in size for working with small amounts of gas. As in other tests, the sample was wet, and within five hours there was an unmistakable evolution of 0.25 cc. of gas, against a slight positive pressure maintained in the apparatus.

Accurate weighing was rendered difficult because of the fact that the filters contained filter paper. Beginning with the eighth experiment, all capsules were allowed to come to constant weight in the balance before final weighing. The most satisfactory agreements were obtained by leaving them in the balance case over night, the case being desiccated by means of conc. H_2SO_4. Agreement between re-weighings was sometimes exact, and lack of agreement was seldom more than 0.0005 g. Exposure in the balance case did not always, if ever, result in a significant loss of weight, for the product from experiments 12 and 13 were made on July 3d, and were reweighed on July 22d, the weights checking exactly in each case. During the intervening time the samples were in colorless glass containers, exposed to diffused light during the day time.

The only analyses made were for the percent of silver in the product, simple heating of which causes a decomposition to form metallic silver. For this decomposition a small porcelain crucible was used. After introduction of the peroxynitrate, two disks of ashless filter paper were pressed into the crucible, the lower disk being about equidistant from the upper disk and from the

peroxynitrate. These disks were cut out and pressed into position with cork borers. After placing the porcelain cover, the crucible was gradually heated in a hot air bath to the charring temperature of paper, and then it was carefully ignited in a blast flame. The papers were used because of the fact that the peroxynitrate decomposes with slight explosions if heated suddenly. They prevented any possible losses from such source.

THE ANODES.

Up to and including the twenty-fifth experiment, the anodes were made of perforated platinum plates. One of the anodes used in earlier work was discarded because of the fact that the peroxynitrate formed less readily on some portions than others; from those portions where the deposit of peroxide was not normal, there was an excessive evolution of gas during the electrolysis. (The word "excessive" is here used in a purely relative sense, for at no time in any of the experiments was gas evolved in more than minute quantities.) Beginning with the twenty-sixth experiment, the platinum anodes were gold plated and burnished, the purpose being to avoid possible catalytic decomposition.

ACIDITY OF SOLUTION.

Beginning with the seventh experiment, a large excess of silver carbonate was always used in all work, and there can be no doubt that the solution was continuously well neutralized.

TEMPERATURE OF SOLUTION.

Experiments 11, 12 and 13 were made with artificial cooling, but no significant changes were noticed, and subsequent work was done at ordinary temperatures.

LIGHT CONDITIONS.

A part of the work was done by artificial light, and some by diffused daylight. No effort was made to carry on any of the work by non-actinic light.

The results of the experiments are given in Table I.

TABLE I.—*Data.*

	Weight of capsule and filter before, grams.	Weight of capsule and filter after, grams.	Weight of capsule with product, grams	Weight of product, grams.	Coulometer gain in grams of copper, No. 1.	Coulometer gain in grams of copper, No. 2.	Weight ratio, peroxynitrate to copper. High.	Weight ratio, peroxynitrates to copper. Low.	Solution strength nitrate.	Current, amp.	Time, minutes.	Percent Ag in the peroxynitrate.
2	7.6707	.....	7.8983	0.2276	0.0874	0.0887	2.60	....	5	0.18	30	.....
3	.....	.....	7.8479	.....	0.1023	0.1022	....	....	5	0.18	30	.....
4	7.1989	.....	7.5062	.....	0.1400	0.1405	....	....	5	0.25	30	.....
5	7.6513	.....	8.0430	0.3917	0.1449	0.1451	2.70	....	5	0.30	25	.....
6	8.1048	.....	8.3658	0.2610	0.1066	0.1067	2.45	....	5	0.25	25	.....
7	7.5899	7.5886	7.7634	0.1748	0.0620	0.0621	2.82	2.80	5	0.075	45	79.39
8	7.1824	7.1819	7.3569	0.1750	0.0623	0.0623	2.81	2.80	5	0.075	45	79.07
9	7.5492	7.5463	7.6777	0.1314	0.0481	0.0479	2.74	2.67	5	0.075	30	79.47
10	7.4255	7.4259	7.6013	0.1758	0.0604	0.0606	2.91	2.90	5	0.075	45	79.08
11	7.5886	7.5881	7.6963	0.1082	0.0396	0.0396	2.73	2.72	5	0.065	30	79.82
12	7.1819	7.1812	7.3585	0.1773	0.0644	0.0643	2.76	2.74	5	0.075	45	79.36
13	7.5463	7.5444	7.7072	0.1628	0.0609	0.0604	2.69	2.64	5	0.075	45	79.35
14	.....	.....	.....	.....	.....	.....	....	....	..	.....	..	.....
15	7.2682	7.2685	7.4482	0.1800	0.0656	0.0659	2.75	2.73	5	0.060	45	.....
16	6.8293	6.8290	7.0903	0.2613	0.0892	0.0891	2.94	2.93	20	0.10	45	79.04
17	.....	.....	.....	.....	.....	.....	....	....	..	.....	..	.....
18	7.1812	7.1816	7.4174	0.2362	0.0800	0.0800	2.96	2.95	20	0.25	15	79.03
19	7.5444	7.5439	7.7333	0.1894	0.0690	0.0639	2.97	2.96	20	0.25	13	79.32
20	6.9311	6.9314	7.1090	0.1779	0.0598	0.0597	2.98	2.97	20	0.20	12	79.17
21	6.8291	6.8290	7.0374	0.2084	0.0708	0.0706	2.95	2.95	20	0.25	12	79.46
22	7.1086	7.1088	7.3164	0.2078	0.0701	0.0701	2.96	2.96	20	0.25	11	79.49
23	.....	.....	.....	.....	.....	.....	....	....	..	.....	..	.....
24	7.5439	.....	7.6926	0.1487	0.0521	0.0521	2.86	2.86	5	0.20	12	79.71
25	7.4249	.....	7.5442	0.1193	0.0419	0.0419	2.85	2.85	5	0.26	10	79.44
26	6.5785	6.5754	6.7126	0.1372	0.0499	0.0500	2.75	2.69	5	0.22	10	79.66
27	.....	.....	.....	.....	.....	.....	....	....	..	.....	..	.....
28	6.5754	.....	6.7326	0.1572	0.0564	0.0561	2.80	2.79	5	0.05	52	.....
29	7.2118	.....	7.3630	0.1512	0.0520	0.0518	2.91	2.90	5	0.05	50	.....

Whenever possible, the weight of a capsule and filter was obtained after the completion of each experiment. It will be noted that positive evidence was thus secured that at least some of the capsules did not change weight appreciably during use.

In this work the greatest emphasis was placed upon the ratio of the weight of peroxynitrate deposited to the weight of copper gained in the coulometer. Since the coulometers did not always check, and there was in some instances a loss of weight of the capsule and filter, two calculations were made, showing the highest and lowest possible ratios deducible from the data in hand.

Because of the sudden interruption of the investigation, analyses were not made of the samples from experiments 28 and 29.

In the study of this whole problem, there are two details which can not receive too much emphasis and attention. Any apparatus which contains a diaphragm or filter for the separation of metallic silver from the anode product is open to suspicion and should not be used unless the apparatus is so transparent and the light conditions so good that all doubt concerning the bipolar action of isolated particles of metal is entirely removed. In earlier work the author obtained anode deposits with silver content up to and in some cases above the theory for Ag_7NO_{11}. After the subtle character of this source of error was recognized, and the apparatus properly modified, no anode deposits contained the theoretical amount of silver for this compound. Also, the evolution of gas from the anode during electrolysis was very slight in all of this work, and had the capsules not been of glass, the gas bubbles could not have been seen. It is very probable that accurate observations of such small bubbles can not be made in opaque vessels such as porcelain evaporators, crucibles and platinum dishes. In these experiments, the total volume of gas evolved during the course of any single electrolysis could not have been more than (estimated) 0.10 cc.; but, there was a positive evolution of gas in all experiments excepting as noted below.

Experiment 28 was the first one during the course of which no gas evolution from the anode could be detected. The anode was gold plated.

The percentage of silver in the deposit is fairly constant, varying only from 79.03 to 79.82, the mean being about 79.37. The

coulometer ratio of compound to copper varies from 2.98 to 2.69 if we take the "high" ratios[16] and from 2.96 to 2.64 if we take the "low" ratios. There is apparently no relation between the fluctuations of the coulometer ratios and those of the silver content. Silver values of 79.44, 79.46, 79.47, and 79.49 correspond to coulometer ratios of 2.85, 2.95, 2.74, and 2.96 respectively. It is a simple matter to eliminate some of the formulas proposed for the peroxynitrate. In Table II are given the percentages of silver, the theoretical number of faradays (96,600 coulombs) necessary to precipitate silver and the theoretical coulometer ratio.

TABLE II.

	Percent Ag	F	Coulometer ratio
Ag_2O_2	87.9	2	3.90
Ag_3O_4	83.5	5	2.44
Ag_2O_3	81.8	4	2.07
$Ag_2O_2.2H_2O$	77.1	2	4.4
$Ag_3O_4.H_2O$	79.7	5	2.55
$(Ag_2O_3)_2.H_2O$	79.1	8	2.14
$(Ag_3O_4)_2.AgNO_3$	79.9	10	2.97
$(Ag_2O_3)_2.AgNO_3$	77.3	8	2.74
$(Ag_2O_3)_3.AgNO_3$	78.8	12	2.52
$Ag_3O_4.Ag_2O_3.AgNO_3$	77.3	11	2.87

DISCUSSION OF RESULTS.

The anode precipitate cannot be a pure oxide because the oxides up to Ag_2O_3 have too high a silver content, and Ag_2O_3 has much too low a coulometer ratio. It cannot be a pure hydrated oxide of definite composition because the coulometer ratios are too low for $Ag_3O_4.H_2O$ and $(Ag_2O_3)_2.H_2O$, for which the silver content is fairly close. We must therefore admit the presence of silver nitrate in the crystals, with or without water. The compound $(Ag_3O_4)_2.AgNO_3$, comes very close to meeting the requirements. In experiments 18-22 in a 20 percent $AgNO_3$ solution with a current of 0.20-0.25 amperes, we get a mean silver content of 79.3 percent instead of 79.9 percent, about 1 percent low, and a mean coulometer ratio of 2.96 instead of the theoretical value of 2.97, which is well inside the limits of error. If we are

[16] Omitting Exps. 2-6 because conditions were not yet standardized.

to consider this as Ag_3O_4 with adsorbed silver nitrate, we must assume an adsorption of well over 20 percent, which seems absurd. That hypothesis may therefore be eliminated. It is difficult to account for the variations satisfactorily, however. Traces of mother liquor in the deposit would cut down the percentage of silver, but it would raise the coulometer ratio. With the 5 percent silver nitrate solution the values for the coulometer ratio are uniformly low without any marked change in the percentage of silver. There seems to be only two ways of accounting for this. We may have an admixture of some substance like $(Ag_3O_4)_2.H_2O$ or $(Ag_2O_3)_2.AgNO_3$ with a low coulometer ratio, or the precipitation at the anode may not be quantitative owing to the solvent action of the nitric acid formed during the run. These experiments do not warrant a final decision between the two hypotheses. Special experiments with this in view ought to clear the matter up, however. In any case, it seems probable that the deposit is essentially $(Ag_3O_4)_2AgNO_3$, which is the composition assigned to it by Mulder, Tanatar, Sulc and Watson.

Baborovsky and Kuzma[17] actually obtained a substance having a composition $(Ag_3O_4)_2.AgNO_3$; but they decided that the silver nitrate was not essential and so they dropped it from the formula. Luther and Pokorny preferred the formula Ag_2O_3; but they say[18] that their experiments are not accurate enough to enable them to distinguish between the formulas Ag_4O_5, Ag_3O_4, and Ag_2O_3. They made no direct analysis and admit that their method does not show whether the oxide is hydrated or not.[19] Their method also does not show whether the oxide contains silver nitrate or not. Their reason for assuming that the oxide contains no silver nitrate is that practically identical values for the electromotive forces are obtained whether one starts with silver nitrate solution or silver sulphate solution. There is no necessary reason, however, why silver nitrate and silver sulphate should have noticeably different effects upon the electromotive forces. Even if the reasoning of Margrete Bose and of Luther and Pokorny were apparently sound, which it is not, it could not stand

[17] Zeit. phys. Chem., **67**, 68 (1909).
[18] Luther and Pokorny: Zeit. anorg. Chem., **57**, 301, 308 (1908).
[19] *l. c.*, 297.

for a moment against the silver determinations which show that the compound cannot possibly be a pure oxide.

The general results of this paper are as follows:

1. An apparatus has been devised which makes it possible to prepare and to collect for analysis silver peroxynitrate with greater accuracy then ever before.

2. Solutions containing 5 percent and 20 percent silver nitrate were electrolyzed with various current strengths. The silver content of the anode deposits averaged 79.37 percent Ag, the limits being 79.03 and 79.82.

3. The ratio of the anode deposit to copper precipitated in the coulometer varied from 2.98 to 2.69.

4. No pure oxide and no hydrated oxide can give both the observed silver content and the observed coulometer ratio.

5. The calculated values for $(Ag_3O_4)_2.AgNO_3$ are 79.9 percent and 2.97, while the values found for electrolysis of 20 percent $AgNO_3$ and a current of 0.20-0.25 amperes are 79.3 percent and 2.96; with 5 percent $AgNO_3$ the corresponding values are 79.4 percent and 2.75.

6. The anode deposit is therefore impure $(Ag_3O_4)_2.AgNO_3$.

7. The low value for the silver content may be due in part to occluded mother liquor or adsorbed silver nitrate; but this would raise the coulometer ratio and therefore cannot be the sole factor.

8. The low coulometer ratio may be due to the presence of some substance like $(Ag_3O_4)_2.H_2O$ or $Ag_2O_3.AgNO_3$. There is nothing in the experiments to show what the admixture is or in what form it is present.

9. The low coulometer ratio may also be due to the anode deposit being dissolved by the solution. Special experiments are needed to determine this point.

10. It requires ten faradays to precipitate one gram molecular weight of $(Ag_3O_4)_2.AgNO_3$.

11. These experiments confirm the conclusions of Mulder, Tanatar, Sulc, and Watson; they are in agreement with the experimental data of Baborovsky and Kuzma, though not with their conclusions. There is no real contradiction with the data of Luther and Pokorny, because these latter are admittedly not accu-

rate enough to warrant any conclusion beyond the one that the peroxynitrate contains a higher oxide than Ag_2O_2.

12. Experiments should be made to determine under what conditions silver nitrate splits off from the peroxynitrate.

Cornell University.

DISCUSSION.

F. C. Frary: In comparison with other elements having a normal valence of one, silver seems to be able to combine with a very abnormal amount of oxygen. This confirms in a way our opinions as to the peculiarities of the valence relations of silver, as for example in the photo-salts.

The accomplishment of such a really accurate piece of quantitative investigation of an inorganic problem treated in a purely chemical way is the kind of thing that ought to be encouraged; we have unfortunately altogether too little of it in current literature.

A paper presented at the Thirtieth General Meeting of the American Electrochemical Society, held in New York City, September 29, 1916, Mr. L. E. Saunders in the Chair.

HIGH TEMPERATURE HEAT DEVELOPED DURING ELECTROLYSIS.

By Carl Hering.

When the current density on a cathode immersed in certain aqueous electrolytes, is increased sufficiently, the cathode becomes red hot and may even melt. Steel can thus be melted electrically while immersed in an aqueous solution.

The purpose of the present notes is to describe briefly some of the properties of this phenomenon and to give some quantitative data obtained from tests. These tests were made only for a preliminary study of these properties and the quantitative data are therefore only crudely approximate.

The explanation of the phenomenon is that with such high current densities the volume of gas formed around the cathode so diminishes the cross section of the conducting liquid between the bubbles that the so-called pinch effect severs what is left of the liquid conductor and keeps it severed by breaking it instantly wherever the liquid and electrode tend to unite again. The film of gas thus formed around the cathode either has an extremely high resistivity, such that the current passing through it develops much heat, or else something of the nature of an arc forms in this film, the difference being that in the latter case there is a transferrence of material through the current path, while in the former there is none; the indications are that the passage of the current through this film is of the nature of an arc. In some respects this film is like that formed in the so-called spheroidal state, when water is dropped on a red-hot plate.

The electrolyte must be one which will develop a free gas at the cathode at these high current densities, which almost any aqueous solution will do. The impressed voltage must of course be high enough to force the current through this film, from 65 to 115 volts in these tests.

The present tests were made with current from a lighting circuit of 123 volts using a bank of lamps in series with the cell. Small strips of thin sheet iron were used as cathodes; the anode was lead, and the solution sulphuric acid of about 1.2 specific gravity. The current through the cell, the voltage at its terminals, and the surface immersed (counting both sides) were measured. Owing to the meniscus and the violent ebullition this surface could be measured only approximately, and as it was small the error due to the three edges and two corners may have been relatively large, as in electrolysis the equivalent of an edge and a corner in terms of a surface, is an unknown factor.

When, with a limited current, a cathode is first immersed deeply so that the usual gasing in the cold state takes place, and is then gradually withdrawn to reduce the submerged surface, a point will be reached when a very sudden change takes place; the current will fall greatly, the voltage will rise greatly, there will be a hissing noise, and the cathode will instantly become red hot, at times melting into globules. The liquid surrounding it also looks red, having the delusive appearance of also being red hot.

If, while thus red hot, the electrode is lowered again very slowly, this high temperature state can be maintained for considerably greater immersions than that at which it started during withdrawal.

By then continuing to lower it, a state is reached without much change in the current or voltage (the current rises and the voltage falls), in which the cathode ceases to be red hot but is enveloped in a distinctly blue film and the hissing is louder. With a still further immersion the conditions change very suddenly again to that of ordinary electrolysis, the current increasing and the voltage dropping, both very greatly. This change occurs when the film breaks and the surface is again wetted by the liquid.

Hence to produce this phenomenon, under the conditions of this test, the cathode must be immersed slowly, only as fast as it becomes heated; the moment the film becomes broken by the surface becoming wetted, the phenomenon ceases. With sufficiently high current densities it will break into this hot state immediately on the closing of the circuit, even when the cathode has previously been immersed.

As the cathodic gas is presumably hydrogen, it was thought that the iron cathode would remain clean and bright. Quite the contrary, however, a thick, black, brittle material forms on it in molten globules, which no doubt is the black oxide, as it is dissolved readily by the current when the film is broken and ordinary electrolysis takes place. The oxygen of this oxide seems to have come from the water, being presumably carried across the film by the arc. Unless this rapid formation of oxide can be prevented, the use of this method for tempering steel objects superficially by opening the circuit after the surface has been heated and while still submerged, would probably not be practicable.

The following data will give a rough idea of the quantitative relations. At about 10 amperes per square centimeter (9290 amperes per square foot) the sudden break from the cold state to the hot state tends to begin, at least under the conditions of this test. The energy at the surface of the cathode before the break, was then being developed at the rate of about 100 watts per sq. cm. (93. kilowatts per sq. ft.), much of which was chemical energy.

When the break occurred the current fell abruptly to about a fifth and the voltage rose more than tenfold. The current density therefore then becomes much smaller, but the surface energy becomes very much greater.

When the current density after the break is about 3.5 amperes per sq. cm. (about 3250 amp. per sq. ft.) the break always occurs, even when the circuit is closed after the cathode is immersed, hence it was not possible to measure it before the break occurred. The surface energy was then being developed at the rate of over 400 watts per sq. cm. (about 370 kilowatts per sq. ft.) which is presumably a far higher heating rate than is developed by a blast flame directed on to a surface.

The following figures will give some idea of what this high rate of heat development means. It is equal to 350 British thermal units, or 78.5 kg. calories, per second per sq. ft. If a kilowatt-hour will melt about 7 pounds of steel, this energy would melt about ¾ pound of steel per second over a surface of 1 sq. ft., and it is likely that most of this film heat goes into the metal and less of it into the water on account of the very high surface resistance of

water. The usual steam boiler practice of evaporating 3 pounds of water per hour per square foot of heating surface, is equivalent to a flow of energy through the walls of the tubes, of about 0.85 kilowatts per square foot; hence 370 kilowatts represent a rate of surface heating about 440 times as great as that in ordinary boiler practice.

During the next state when the cathode becomes cooler and is enclosed in a blue hissing envelope, the current density was about 4 amps. per sq. cm. (about 3700 amps. per sq. ft.) and the energy development at the surface was about 270 watts per sq. cm. (about 250 kw. per sq. ft.) showing that the current density was then a little higher than during the red hot state, but the surface energy development was considerably less, hence the cathode was cooler.

When the current density during the latter state is then still further reduced by deeper immersion, to about 2. to 2.5 amps. per sq. cm. (about 1900 to 2300 amps. per sq. ft.) and the surface energy to about 130 watts per sq. cm. (about 120 kilowatts per sq. ft.), the film breaks, the cathode becomes wetted and ordinary gasing in the cold state sets in. Hence roughly about 100 kw. per sq. ft. is the breaking point either way. Being caused by the pinch effect, current densities may not be the criterion in this phenomenon.

A rough test was then made in which the electrode to be heated was made the anode. Only by barely touching the liquid with the anode could any high temperature effects be produced, and even then only the corners became visibly red; with a further immersion the film always broke. The voltage before the break was about 117, very nearly the maximum available, and even this gave less than half an ampere; with a higher voltage better results could no doubt be obtained. The current density was, as nearly as could be estimated, about 4 amps. per sq. cm., hence about like that with the cathode, but the energy development was over 450 watts per sq. cm., hence higher than with the cathode. This may be due to the fact that only half as much gas is developed per ampere at the anode than at the cathode, or if an arc is formed through this film it may mean that the current traverses the arc more easily from liquid to electrode than from electrode to liquid.

The metal of this anode was eaten away slightly at the edge and was coated with a red layer, presumably the lower oxide, though sometimes it was left gray and bright. It did not seem to be dissolved however as fast as would be expected.

The curious fact that the cathode apparently becomes very strongly oxidized when thus heated, interferes with using this method for the surface hardening of steel objects; but with higher voltages it might be possible to heat so rapidly, perhaps in a few seconds, that the oxidation during that brief time might not be serious.

As this method enables one to heat a surface far more rapidly than it can be done by means of a flame, it may become possible to heat a surface to a high temperature so quickly that the heat would not penetrate into the interior until after the object of the heating has been accomplished, as for instance in alloying a surface with a metal which has been plated upon it. The heat is also more evenly distributed over a complicated surface than is possible with a flame, and the temperature is not limited like in combustion heat.

If it should be true that the passage of the current through this film forms a true arc, then it would seem to follow that the true electrolytic action takes place on the liquid side of the film, which would mean that the real cathode then is the film of hot gases and not the metal. The conditions would then be similar to when an arc is struck between a carbon rod and the upper surface of an electrolyte, in which the question also arises what the real electrode is at which the electrolysis takes place. Unipolar electrolysis would be contrary to our present conceptions.

DISCUSSION.

E. F. Northrup: I think the Society is indebted to Dr. Hering for bringing this phenomenon to its attention. I suppose the mere fact that electrodes immersed in electrolytes would get hot by passage of a heavy current has been well known, but Dr. Hering has called attention to the nature of the phenomenon in considerable detail. This appears to me to be another case of very interesting matters developing when note is taken of the forces with which we deal when these are carried to extreme limits. Thus, the "pinch

effect" phenomenon, and all the important attendant consequences of its study, was discovered accidentally by attempting to push current densities to much greater magnitudes than are ordinarily used.

It has been my experience that almost any phenomenon if studied and investigated quantitatively will be almost sure to develop some interesting feature other than that looked for, and that commercially important as well as scientifically interesting results may be obtained. Thus would it not be interesting to modify the experiment made by Dr. Hering and observe what would happen when passing a very heavy current from tungsten or molybdenum metal into a fused salt? Possibly the tungsten or molybdenum electrodes might be made to alloy with the base of the fused salt.

I hope Dr. Hering will study the phenomenon described by him further and obtain quantitative results.

C. G. Fink: I do not believe that a paper on the Wehnelt interrupter has yet been published in our Transactions. Much has been done on that subject, and it would be interesting to extend the work of Dr. Hering and see whether the various thories could be brought together. Dr. Hering said that the cathode would oxidize; has he tried out organic solvents? There are a number of organic liquids which are fairly good conductors.

Carl Hering: I tried nothing but sulphuric acid, sodium hydrate and some metallic salts, because I was after certain results. This was not a research, I simply have gathered this data together, thinking that it might be of interest to others just as it is. The Wehnelt interrupter is unquestionably a pinch-effect phenomenon.

I am inclined to believe, as Dr. Northrup states, that further study of this phenomenon, particularly in the direction of non-aqueous electrolytes, like fused salts (which had suggested itself to me too) might be of considerable interest and might lead to something of value. If I had the opportunity I would be glad to go further into this investigation. One drawback is that for larger surfaces it takes quite a lot of power; although used for only a short time, yet the capacity to give that power for that time must be available.

F. C. Frary: To many of us Dr. Hering's hope of avoiding oxidation of the iron is not well founded, for the reason that if you produce heat enough on that metal to melt ¾ lb. (0.34 kg.) of steel per second you must absorb most of this heat in the water, with the resulting production of a quantity of steam, and it is this steam that reacts on the iron at red heat. The small amount of hydrogen would have no effect whatever in retarding that action.

Carl Hering: I said in the paper that the oxygen no doubt came from the steam.

F. C. Frary: If you have to do it in an aqueous solution you cannot get away from the steam.

With regard to the fused salts, that phenomenon has been investigated, and the anode effect in fused salts has been the subject of papers read before this Society and also at other places. It is well known in the electrolysis of fused chlorides, for example. If you get the anode temperature high enough to expand the gas to a sufficient extent, you will get the phenomenon of an arc across the gas, and produce higher temperature, and expand the gas still further, thus raising the lower limit of anode current density. As Dr. Hering indicated, the effect is not directly a function of the current density, but depends more on the temperature of the actual surface utilized than anything else. It is a gaseous phenomenon, and you get true electrolysis, producing chlorine.

W. R. Mott: I believe that Dr. Hering has done us a great service in bringing this phenomena to our attention because there are probably many practical applications of it that can be worked out in this rather unique way of getting a metal white-hot by merely placing it in a sulphuric acid solution and using it as cathode at high density of current. As I recall, Sir Humphrey Davy and Faraday did the first experiments along these lines. Several years ago Prof. Burgess made the experiment and figured out the wattage. He calculated at that time that the cost of power was considerably greater than that of welding by other means. But there are special cases, as pointed out by Dr. Hering,

that make this process of value. Considering oxidation, the volume of hydrogen and use of metal as cathode should tend to reduce it.

Speaking of arcs in liquids, I have tried a few experiments on flame arcs both in water and in aqueous solutions, and I could get an excellent flame arc, although it was rather short and small.

CARL HERING: Dr. Northrup suggested using solutions containing metals. In that connection, I might say I tried it, but could not take time then to carry it to a conclusion; I am still of the belief that something useful or interesting might be accomplished in this direction. For instance, taking a zinc solution and first depositing some zinc by a low current density without regard to whether it is crystalline or spongy, the current density might be suddenly increased to these heating values, for a few seconds; in this way the deposit might be immediately alloyed with the article that is coated, and it may be possible in this way to galvanize or cover a metal with another metal, which alloys with it, in the course of a few seconds.

J. W. RICHARDS: In the electrolysis of fused salts a phenomenon quite analogous to this is of frequent occurrence at the anode. In the electrolysis of the aluminium bath, there is a gas escaping continuously around the carbon anode, mostly CO mixed with some CO_2, and there is an appearance of minute arcs at the surface of the anode. It is almost impossible to get regular electrolysis going until these arcs subside and become almost invisible.

There seems to be the phenomenon which Mr. Hering has spoken of, analogous to the spheroidal state, occurring when you have high voltage and electrolyze a fused salt. You can easily pass from a state of continuous smooth electrolysis at 6 or 8 volts, to one where you can absorb 20 or 30 volts, and that absorption is evidently at the anode, where the little arcs are formed. This appears also to coincide with the fact that at low voltages the electrolyte is drawn toward the anode, and at high voltages the electrolyte seems to be repelled from it in a form analogous to the spheroidal state. The phenomenon has not been studied as it ought to be. You can see it referred to, however, in nearly all laboratory accounts of experiments on electrolysis of fused salts.

E. E. F. CREIGHTON: This same phenomenon is used in lightning arresters, and it carries the voltage, perhaps, a little further than Dr. Hering. If one continues to push the current, the voltage will go up at least 2000 volts, and we use that as the unit in a lightning arrester to extinguish the dynamic arc after the lightning has passed.

F. C. FRARY: With regard to Dr. Hering's question about the anode effect in fused salts, if you will refer to the paper of Mr. Badger and myself, in volume **16** of the Transactions of this Society, you will find the voltage discussed and charted, and voltages as high as 70 shown, which are easily obtained by any one. We had not been electrolyzing under ideal conditions, and our normal voltage was 17, but the true reversible decomposition voltage for calcium chloride would be not far from that of sulphuric acid. The whole phenomenon is exactly analogous to the simple formation of an arc through a highly-heated gas layer, and, as has been stated, it is also analogous to the spheroidal state, the highly-heated gas layer being continuously evolved from a hot liquid surface. You will find many other references to that sort of phenomenon in Allmand's "Applied Electrochemistry," p. 164.

CARL HERING: If Dr. Frary got as high as 70 volts, he undoubtedly encountered the same phenomenon but, in the case of the aluminum baths in series, I do not think the phenomenon could occur on account of the limitations of the generator.

J. W. RICHARDS: In the aluminium bath, the bath may be working normally, at 7 or 8 volts. When the supply of alumina in the bath is exhausted, and oxygen is not evolved at the anode, but probably fluorine in its place, the voltage may go up inside of a few seconds from the normal voltage up to 25 or 30. The bath being one of a series, the voltage may accumulate right on that bath, and even burn out the indicating lamp, which usually gives no light at the usual voltage absorbed by the bath. Before the workman can get to it, inside of five seconds, sometimes, the voltage may jump to 25 or 30 volts. This phenomenon is connected with the change in the nature of electrolysis, and it indicates the exhaustion of the alumina in the bath, for the voltage

is brought down immediately by stirring in alumina, and thus changing back the composition of the bath.

F. C. ATWOOD: I would ask Dr. Hering if he ever observed an actual transition or transference of metal from the electrodes into the bath? In the preparation of Bredig solutions of metals, an arc is struck under water and you get an actual colloidal solution of the metal which you are using as an electrode. In this case you have an arc containing metallic vapors, and, when they are suddenly cooled by the electrolyte, they form small particles of matter of colloidal dimensions.

CARL HERING: We have all no doubt produced colloidal solutions of metals in this way, but that is a case of striking an arc between two solid electrodes under a liquid, and that is rather different matter, as it is not electrolysis but merely a condensation of high-temperature vapors.

Replying to several remarks, no claims are made in the paper that this phenomenon had never been noticed before, though I do not recall seeing any earlier description of the quantitative analysis such as I have given, but I am inclined to believe that in some of the cases cited in the discussion the phenomenon was a different one.

A paper presented at the Thirtieth General Meeting of the American Electrochemical Society, held in New York City, September 29, 1916, Mr. L. E. Saunders in the Chair.

THE POSSIBILITIES OF DEVELOPING SUPER-REFRACTORY MATERIALS FOR INCANDESCENT LIGHTING

By F. A. Fahrenwald.

It seems to be generally conceded by electrical and illuminating engineers, that the upper limit of temperatures at which incandescent lamps may be used is fixed by the practical operating temperature of the tungsten filament. This prevailing sentiment is expressed in a recent paper by an eminent engineer, from which the following is quoted:

"Can we find a material, a metal, having a higher melting point than tungsten? Doubtless it must be an element, because for chemical reasons the melting point of any compound of two materials must be somewhere between that of either of the metals entering into it. For example, all tungsten compounds must necessarily have lower melting points than tungsten itself, all carbon compounds have lower melting points than carbon, and so on."

It is the object of the present paper to offer a few analogies in answer to this all-important question, and to outline approximately the boundaries of fields in which proper research may produce materials more refractory, or possessed of greater thermal stability, than any substance at present available.

In the list of known elements there is not one that alone will prove a serious competitor of tungsten for lamp manufacturing purposes.

In view of this, it is evident that any search for the desired material must deal with combinations of elements, for it is known that the physical properties of many elements may be radically changed by adding to them certain amounts of another element, or of several elements.

The combinations of metallic with non-metallic elements have been extensively studied, and the general properties of these

compounds are well defined. No substances of this type, however, have been found satisfactory in this connection, although the oxides of calcium, magnesium, and similar metals, have found wide application in cases where heat may be applied externally. The oxides of thorium, zirconium, and cerium have been found especially satisfactory when used in the Nernst glower, or in the Welsbach mantle. None of these, however, can rival the ductile tungsten filament for illuminating purposes. On the whole, it is not likely that oxides, or other refractory salts, will replace the tungsten filament type of lighting element.

The conditions under which electrically heated filaments may be operated, however, allows another field to be considered—one that has as yet received very little attention with this end in view —that of inter-metallic combinations. Many experiments have been performed, in which composite metallic filaments have been made, but in all cases only such materials have been added to the refractory component as would be readily volatilized on heating, and so in this way produce the single component filament.

The use of thoria (Coolidge Patent)—although a non-metal—is an exception, however, but here the foreign substance is inert, and acts only physically, in preventing undesirable crystallizing phenomena. The melting point and volatilizing tendencies of the tungsten are not altered.

Inter-metallic combinations may be divided into several distinct classes, and in order to define the limits of possibilities in this application, it will be necessary to consider first, very briefly, inter-metallic relations in general.

There is no difference in principle between reactions which take place at very high temperatures, resulting in alloys, and those which take place under ordinary conditions, as, for instance, in the course of an ordinary chemical analysis. All reactions and conditions of equilibrium are governed by the same rules, and the same types of constituents result in both cases.

When two or more metals are brought together in the liquid state, or fused together, the conditions resulting are similar to those found when two or more ordinary liquids are mixed. When the temperature is lowered, the solidified mass may contain one of the four following constituents: pure component, solid solution, compound, or eutectic—or some combination of these.

A comparison of the properties of different alloys containing these constituents has shown that they impart their characteristic properties to the alloy of which they form a part; in fact, the relation between the constitution of an alloy and its physical properties is so clearly defined, that the possibilities of industrial application may be predicted for a given alloy, if its constituents are definitely known. Conversely, if a certain application is desired, as in the problem under consideration, a definite limit may be placed upon the number and amount of constituents permissible.

Fortunately, the number of constituents is limited to four, as given above. Pure metals impart their own characteristics to the alloy of which they form a part. *Solid solutions* are, in general, the ductile constituents (if formed of ductile metals, or of a preponderance of one ductile metal). The solution of a metal (or compound) in another metal increases the hardness, and usually the strength, of the solvent. The *vapor pressure is lowered* in certain cases, and the electrical conductivity is always lowered. The melting point curve of a solid solution series lies usually between values representing the melting points of the pure components, although a minimum is possible, as in the case of alloys of copper with gold or manganese.

The melting point of the more refractory component is, in general, not lowered so rapidly by the addition to it of certain amounts of the more fusible component, as the melting point of the latter is raised by the addition to it of like amounts of the former; the curve being usually convex upwards.

Inter-metallic Compounds are almost invariably brittle, and if present in sufficient quantities in an alloy in which it is insoluble, destroys its ductility. If a compound more refractory than either component is formed (which is a common occurrence), and if this be soluble in the more refractory component, then quite ductile refractory solid solutions are possible. Many inter-metallic compounds possess melting points several times as high as either component, which is true also of non-metallic compounds; a fact which at once answers part of the question quoted at the beginning of this article. Many of these compounds are very stable at their melting temperature, if enclosed in a proper atmosphere.

Eutectics are hard and brittle, and possess melting points lower than either of their components, and even when present in very small amounts, tend to solidify between the grains of the alloy, thus destroying its ductility.

Of the various possible types of alloys, then, only solid solutions and compounds may profitably be considered in a search for more satisfactory incandescent lighting materials.

It is very probable that solid solution alloys of tungsten will be developed, which will possess a lesser tendency to volatilize at high temperatures than does the pure metal, for it is a known fact that the vapor pressure of a metal solvent is lowered by the addition of a metallic solute, when a V-type melting point curve results, in the same way as is that of an ordinary liquid by the solution of a salt. Certain refractory elements may serve for this purpose, as tantalum, osmium, or perhaps some refractory compound of tungsten itself.

In many cases the melting point of a metal is lowered but very little by the solution in it of another metal, and if such a condition should accompany lowered vapor pressure, a greater thermal stability will result, thus enabling higher temperatures to be employed than are now practicable.

The field of intermetallic compounds among such elements as tungsten, molybdenum, tantalum, osmium, and similar metals, is more attractive, however, for the reason that cases of very refractory compounds are very common between metals of lower melting point; occurring, in fact, at all temperature ranges below the upper limits which have been reached in past alloy investigations.

A complete list of the known elements, as given for 1915, includes eighteen that melt above 1700° C. In this refractory group there exists a record of only one complete binary investigation.[1]

Several of these elements have been combined in relatively small proportions with metals of lower melting point; *e. g.*, tungsten, molybdenum, and vanadium, in steels, or, with nickel or cobalt; but of this refractory group, platinum is the only one that has been extensively studied in this connection.

[1] The System Molybdenum—Tungsten. F. A. Fahrenwald, June, 1916, Bulletin of the American Institute of Mining Engineers.

When one considers that with few exceptions the industries have made use of alloys, to the exclusion of pure metals, it is reasonable to expect that alloys of this refractory group will serve in cases where the pure metals find no application.

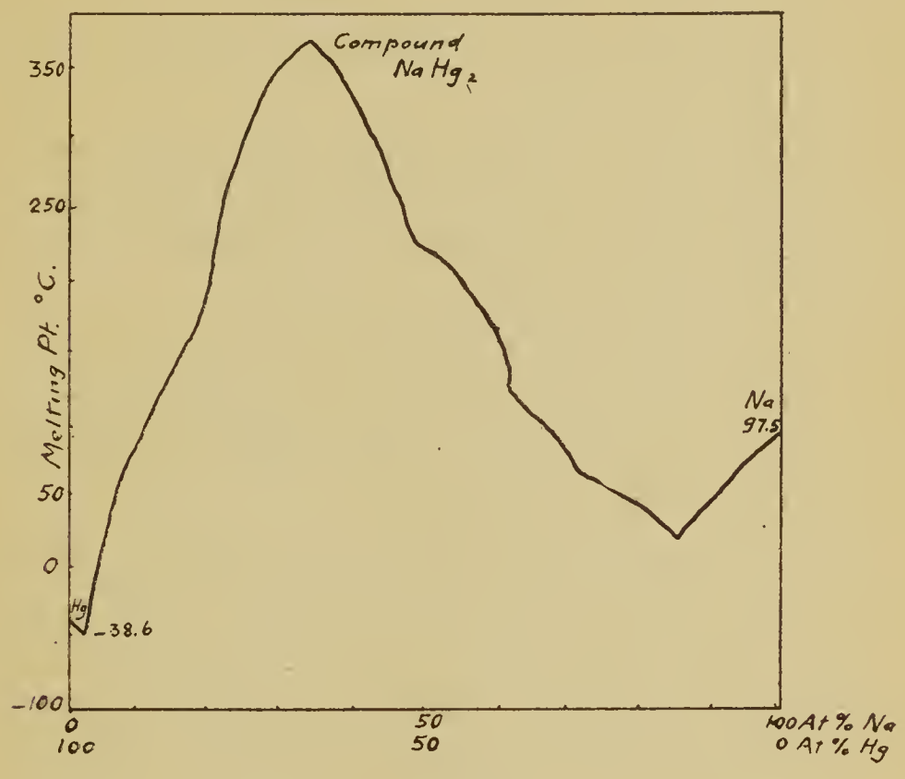

FIG. 1.

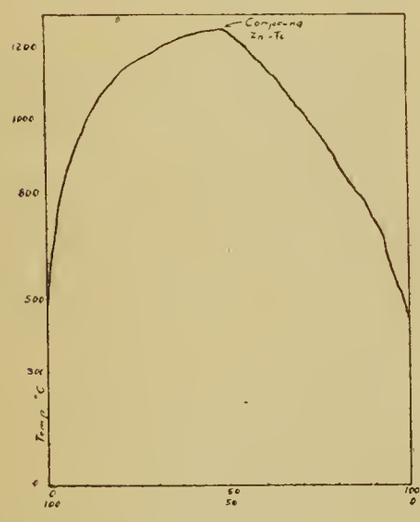

FIG. 2.

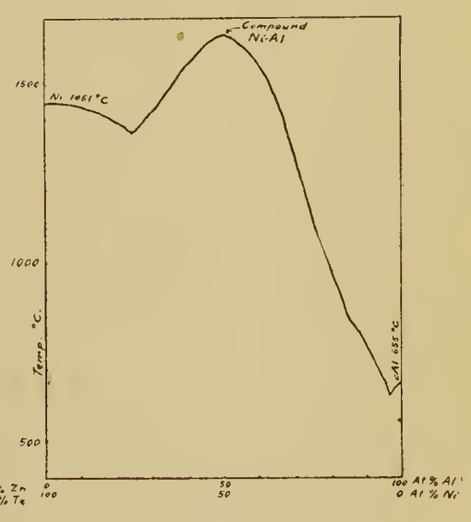

FIG. 3.

Several series of alloys in which compounds occur that possess melting points above those of their component metals, will serve as examples of the type of super-refractory compounds that may be developed by alloy research in the field of refractory metals.

The mercury-sodium series (Fig. 1) is a good example, at low temperature ranges, of this type of alloy. Mercury itself melts at —38.6° C., sodium at 97.5° C., but an alloy of the two containing these elements in the proportions represented by the chemical formula $NaHg_2$ melts at 360° C.; nearly four times as high Centigrade as does the more refractory component (or nearly twice on the absolute scale).

The melting point curve (Fig. 2) of the tellurium-zinc series shows a compound of the formula ZnTe which melts above 1200° C., while the melting points of the pure elements themselves are 421° C. and 419° C., respectively.

At still higher ranges, the melting point curve (Fig. 3) of the nickel-aluminum series shows a compound of the formula NiAl which does not fuse below about 1640° C., nearly 200° C. above the melting point of nickel.

It is not at all improbable that an investigation of the more refractory metal alloys will reveal a binary series possessing a melting point curve with a maximum similar to that shown on these three typical examples. Even if this should extend only a few hundred degrees above the melting point of tungsten, the fact that lighting efficiency does not vary directly, but as a higher power of the temperatures employed, would make a material of this nature of very great value.

It is possible also that alloys of this nature would possess more favorable radiation characteristics than those of tungsten.

In conclusion, then, there is no reason to believe that proper alloy research will not develop a material for refractory, electrical-resistance, lighting elements which will be more efficient than pure tungsten.

This material will probably be one of the following:

1. A super-refractory inter-metallic compound.

2. A solid solution alloy of a refractory metal, possessing lower vapor pressure than tungsten.

3. A refractory alloy having more favorable radiation characteristics than has pure tungsten.

DISCUSSION.

M. G. Lloyd: There is one other possibility of finding a more refractory substance than tungsten for this purpose, and that is the discovery of an element with higher melting point. When the elements are listed according to the periodic system there is an indication that a metal exists, which is at present unknown, which would have a higher melting point than tungsten, and perhaps we may hope that it will some day be discovered and supersede tungsten for that purpose, giving better luminous efficiency.

W. R. Mott: I understand the last gentleman to refer to the possible periodic element indicated by Steinmetz (page 77) in his book on Radiation, Light and Illumination. This is a very interesting possibility although admittedly a rather remote one.

This paper interests me especially from the standpoint of high-temperature arc chemistry. For stable high-temperature materials, I consider of importance for prediction the intensity factor of the heat of formation, other conditions being equal. Again, in the matter of composites, the behavior of vanadium toward either oxygen or carbon is unusual, because the pure metal is of lowest melting point while there is a rising curve on either side. (See Ruff and Martin, Zeit. f. angew. Chem. (1912) **25**, 39.)

Percent Oxygen	Melting Point	Percent Carbon	Melting Point
31.92	2000° C.	1.15	1863° C.
25.77	1935° C.	2.69	2185° C.
15.96	1828° C.	4.41	2375° C.
2.36	1734° C.	9.29	2675° C.
Cal. pure vanadium	1715° C.	19.01	about 2750° C.

Thorium oxide and tungsten might have a similar effect, although I believe that scandium oxide (Sc_2O_3) also would have unusual stability and might have even a more favorable surface tension effect. In the case of thorium oxide, its boiling point is probably near 5000° K., like tungsten. In the matter of boiling points several oxides and metals are much higher than carbon which, however, continues to maintain its unique position as the substance remaining solid to a higher temperature than any other substance whatsoever. Of the oxides (those remaining solid at 2500° C.), there are only three, beryllium oxide (BeO), yttrium oxide (Yt_2O_3) and zirconium oxide (ZrO_2). (The scandium

oxide has promise, but has not been adequately tested.) A few very rare oxides are suggested in Hutchinson's book. (See page 39, High-Efficiency Illuminants and Illumination.)

JAMES AUPPERLE: The last gentleman who spoke mentioned the fact that the addition of oxygen to vanadium raised the melting point. It is well known that most metals will only combine with a very small amount of oxygen. For instance iron will combine with but 0.2 percent. What would be the utility of a metal that would be mechanically mixed with oxygen as far as its physical properties are concerned?

C. G. FINK: The subject of Mr. Fahrenwald's paper is a very interesting field for research. Mr. Mott's suggestion to try scandium with tungsten is a very good one, and I would like to know where he keeps his supply of scandium.

W. R. MOTT: There is a very excellent article on scandium published by Meyer (Zeit. für. anorg. Chem. **86**, 257, 1914) in which it appears that fair amounts of scandium have been extracted.

A paper presented at the Thirtieth General Meeting of the American Electrochemical Society, held in New York City, September 29, 1916, Mr. L. E. Saunders in the Chair.

COMPARISON OF THE IONIZATION CURRENTS DUE TO EQUAL QUANTITIES OF RADIUM EMANATION IN DIFFERENT TYPES OF ELECTROSCOPES.

By T. H. Leaming, Herman Schlundt and Julius Underwood.

Small quantities of radium are usually estimated by the emanation method. The emanation produced by the radium in the sample of material to be analyzed is separated quantitatively and introduced into a standardized electroscope. When the potential of the electroscope is sufficiently high to prevent recombination of the ions the current produced, measured by the rate of discharge of the instrument, is proportional to the quantity of emanation present. Knowing then the quantity of emanation corresponding to unit rate of discharge, a quantitative determination is obtained by simply multiplying the observed discharge rate by the calibration constant of the instrument.

The electroscopes are generally standardized by introducing known quantities of emanation which may be conveniently obtained from weighed samples of pitchblende, whose uranium content is known, or from suitable volumes of a standard radium solution. Becker[1] has suggested the name *emanometer* for a standardized emanation electroscope.

To obtain the actual values of the ionization currents that correspond to different rates of discharge of the electroscope, another calibration constant is required. The electrostatic capacity of the instrument must be known as well as the potential corresponding to the different scale readings. The ionization current, I, expressed in electrostatic units is then deduced by the well-known formula

$$I = \frac{C\ V}{300\ t} \qquad (1)$$

[1] Zeit. Instrumentenkunde, 30, 293 (1910).

where C represents the electrostatic capacity in cms., and V the fall of potential in volts observed during *t* seconds. Dividing by 300 reduces volts to electrostatic units of potential. The electroscope then becomes an electrometer, and if the calibration constant also expresses the emanation that is required to produce the unit current, the instrument will again serve as an emanometer.

Since the emanation is distributed throughout the space of the ionization chamber, some of the alpha particles will not have their maximum range in air—4.16 cm. at 15° and standard pressure—and consequently the ionization current measured will not represent the maximum ionization the radiations are capable of producing. Moreover the number of particles whose ionization path is reduced by the walls of the chamber will depend upon the size and shape of the instrument. Evidently then the ionization currents due to equal quantities of emanation in different types of ionization chambers will have somewhat different values.

Duane,[2] and later Duane and Laborde[3] deduced an empirical formula for the ionization currents resulting from equal quantities of emanation in three sizes of cylindrical ionization chambers. Randall[4] in his investigation of the Boltwood standard of radioactivity reached the conclusion that for small electroscopes of the same design the observed ionization current is nearly proportional to the volume of the ionization chamber. The relation of Duane and Laborde involves both volume and surface factors. The general equation is,

$$I = K - K^1 \frac{S}{V}$$

which may also be written in the form,

$$I = K\,(I - C\,S/V) \qquad (2)$$

The factors K and C are constants. The numerical value of K will depend upon the quantity of emanation that is made the reference unit. The constant C is a fraction and may be designated the reduction factor. When the ionization current is measured at the time it attains its maximum value—about three hours after the introduction of the emanation—both constants have higher

[2] Compt. rend., **140**, 581, 786 (1905); Jour. d. Physiq. (4) **4**, 605 (1905).
[3] Compt. rend., **150**, 1421 (1910).
[4] Thesis University of Missouri, 1901, Trans. Am. Electrochem. Soc., **21**, 463 (1912).

values, the increase in ionization being due to the active deposit of rapid decay—RaA, RaB, and RaC. The constant K was determined by Duane and Laborde for the quantity of emanation produced per second by one gram of radium (element). These investigators found that the ionization current due to one gram second of emanation alone is expressed by the equation,

$$I_0 = 5.19 \left(1 - 0.517 \frac{S}{V}\right) \qquad (3)$$

The maximum value of the current measured three hours after the introduction of the gas into the chamber is given by the relation,

$$I_{(max)} = 13.15 \left(1 - 0.572\ S/V\right) \qquad (4)$$

The measured and calculated values show almost perfect agreement for the three ionization chambers employed. The unit quantity of emanation produced a current of 4.45 e. s. units in the large chamber, 37.5 cm. high, diameter 18.5 cm., and a current of 3.11 e. s. units in the small chamber 13.5 cm. high and 6.7 cm. in diameter. The current due to emanation alone, in the large chamber, thus exceeds that measured in the small one by 43 percent, and the maximum ionization current of 11.04 e. s. units in the large chamber exceeds that in the small one of 7.25 units, by 52 percent. The results illustrate in a striking manner the differences in currents produced by equal quantities of emanation in different sized ionization chambers of the same design, and whose dimensions lie well within the range of variation of different types of standard electroscopes used in radioactive measurements. This point will be further emphasized by an example from Randall's[5] measurements. He found that the emanation in equilibrium with one gram of uranium gave an ionization current of 2.36×10^{-10} amperes in a rectangular ionization chamber whose volume was 590 c.c., and a current of 4.80×10^{-10} amperes in a cylindrical condenser whose capacity was 2840 c.c., a ratio of 1 to 2. On the other hand, equal currents of 4.8×10^{-10} amperes were obtained in two chambers, the one rectangular, volume 952 c.c., the other cylindrical and having a volume of 2840 c.c.

Duane and Laborde also found that equations 3 and 4 above

[5] *Loc. cit.*, p. 494.

applied to a cylindrical ionization chamber whose height was only 0.6 of its diameter. If we assume that the formulas of Duane and Laborde apply to all ordinary types of cylindrical chambers then it follows that the number of gram-seconds X of emanation producing the observed ionization current I, measured at maximum, is computed by the equation

$$X = \frac{I_{(max)}}{13.5\ (1 - 0.572\ S/V)} \qquad (5)$$

for any electrometer when its dimensions are known. The formulas of Duane and Laborde thus offer a direct means of converting observed ionization currents into gram-seconds of radium, and a number of investigators[6] have made use of these formulas in connection with radium determinations.

As above stated, the constant K in the formulas of Duane and Laborde refers to the quantity of emanation produced by one gram of radium per second. When radium and the emanation attain equilibrium, the quantity of emanation transformed per second equals the quantity produced. Now, since the emanation in equilibrium with one gram of radium (element) has been adopted as a standard and designated the curie, the gram-second of emanation, representing its rate of transformation, is the radioactive constant, $\lambda = 2.085 \times 10^{-6}$ secs. and therefore the equilibrium quantity, the curie is the reciprocal of the radioactive constant, or $1/\lambda$; that is, the curie equals $1/\lambda$ gram-seconds of emanation or 4.795×10^5 and this is the conversion factor of ionization currents per gram-seconds of emanation to currents per curie. Introducing this constant into the formula of Duane and Laborde, we obtain the following expressions for current due to one curie of emanation alone in cylindrical ionization vessels.

$$\text{Current per curie of emanation} = 4.795 \times 10^5 \times 5.19\ (1 - 0.517\ S/V)$$

$$\text{or } 2.49 \times 10^6\ (1 - 0.517\ S/V) \text{ e. s. units.} \qquad (5)$$

Likewise the maximum current after a lapse of three hours will be

$$\text{Max. current per curie} = 6.31 \times 10^6\ (1 - 0.572\ S/V) \text{ e. s. units} \qquad (6)$$

[6] See Becker, Zeit. Instrkund., **30**, 293 (1910); Ramsey, Indiana Academy of Sciences, 1912-14, 453; Engler, Sieveking and Koenig, Physik. Z., **15**, 441 (1914). Schmidt and Nick, Physik. Z., **13**, 199 (1912).

The actual number of alpha particles expelled per second per curie[7] is 3.57×10^{10}, and since each alpha particle produces 1.74×10^5 pairs of ions along its path in air, each ion bearing a charge of 4.65×10^{-10} e. s. units, the total ionization current that one curie of emanation is capable of producing is given by the products of

$$3.57 \times 10^{10} \times 1.74 \times 10^5 \times 4.65 \times 10^{-10} \text{ or}$$
$$2.89 \times 10^6 \text{ e. s. units} \qquad (a)$$

From the measurements of Duane and Laborde we find the current due to one curie of emanation alone, in the large chamber, has the value of 2.18×10^6 e. s. units, and in the small chamber, 1.49×10^6 e. s. units. The ionization efficiency[8] of the chambers is then $2.18 \times 10^6 / 2.89 \times 10^6$ or 75 percent in the large vessel and 51 percent in the small one.

Likewise we may deduce the total current due to the alpha particles expelled from one curie of emanation and its transformation products RaA and RaC at the time that measurements are generally made, three hours after the introduction of the emanation: The quantity of emanation remaining from one curie after three hours is 0.978 curie; the quantity of RaA will be 0.978 curie, whose ionizing effect will be equivalent to 0.489 curie since RaA and RaC are solids and therefore one-half of their radiation is absorbed by the walls and electrodes of the ionization chamber. After three hours RaC has not quite attained equilibrium, 98 percent of the equilibrium quantity being present.[9] Hence its ionization effect will be equivalent to 0.479 curie. Since the number of ions produced in air by a single alpha particle from Ra Em, Ra A, Ra C is respectively, 1.74×10^5, 1.88×10^5, 2.37×10^5, the total ionization current at the time of maximum due to Ra Em, Ra A and Ra C is summed up in the expression $(0.978 \times 1.74 + 0.489 \times 1.88 + 0.479 \times 2.37)\ 10^5 \times 3.57 \times 10^{10} \times 4.65 \times 10^{-10}$ which gives 6.24×10^6 e. s. units.

Assuming that the ionization due to the beta and gamma rays is approximately one percent of the total, we see that the total current that one curie of emanation and its decay products is capable of producing at the time of maximum activity is 6.3×10^6

[7] Rutherford, Phil. Mag., 28, 320 (1914).
[8] A term introduced by Randall, *loc. cit.*, p. 495.
[9] Makower and Geiger, "Practical Measurements in Radioactivity," p. 144. Book published by Longmans, Green & Co. (1912).

e. s. units. It is interesting to note that this number is the value of K in the formula of Duane and Laborde for maximum current. (Equation 6).

The second term in the general formula, then represents the decrease in the theoretical maximum current due to reduction in range of the alpha rays by the walls and electrode of the ionization chamber. It was this consideration that prompted us to speak of the second constant in the formula of Duane and Laborde as the reduction factor of the instrument. Is the value of this second constant the same for all ordinary cylindrical ionization chambers, or does it assume special values? Can the same factor be used when the ionization chamber has a rectangular or spherical form? Our experiments deal with these questions. Our results indicate that the reduction factor has specific values for different types of electroscopes, and that it is variable even for cylindrical chambers with divergence of their relative dimensions from the sizes tested by Duane and Laborde.

It may be noted in passing that the maximum ionization currents measured by Duane and Laborde when expressed per curie are respectively 5.3×10^6 and 3.48×10^6 e. s. units for the large and small chambers, corresponding to ionization efficiencies of 86 and 56.5 percent. Randall[10] reports ionization efficiencies for maximum currents for the three types of electroscopes used that range from 39 to 79 percent. Randall deduced the total maximum current for his electroscopes on the basis of the McCoy uranium standard. He states that the emanation in equilibrium with one gram of uranium produces 1.854 e. s. units. We can express this value per curie by multiplying by the uranium : radium ratio,[11] 3.1×10^6U : 1 Ra, i. e. 1 U to 3.23×10^{-7} Ra. The product is 5.75×10^6 e. s. units, a value eight percent lower than by our method of calculation.

The foregoing citations will serve to illustrate the value and importance of applying the formula of Duane and Laborde when attempts are made to translate the activity of water and gas samples for example, expressed in electrostatic or Mache units[12]

[10] *Loc. cit.*, p. 467.

[11] Rutherford, Phil. Mag., 28, 320 (1914).

[12] One e. s. unit of current equals 1000 Mache units. The activity of a water gas sample expressed in Mache units represents 1000 times the total current in e. s. units the emanation alone per liter is capable of producing.

into grams of radium or curies, and vice versa. The equations enable one to convert ionization currents into curies without determining experimentally the radium equivalent of unit current for the particular electroscope, and conversely the radium calibration constants of electroscopes may be translated into ionization currents when the electrical constants of the instruments are not known.

SCOPE OF EXPERIMENTS.

In investigating the radioactive properties of natural waters[13] and gases, our practice has been to standardize electroscopes with known quantities of radium emanation and to determine in addition the electrostatic capacity of the instruments and the potentials represented by scale readings. We have thus been able to express activities directly as grams of radium (curies), and in terms of electrostatic units of current and Mache units without depending upon the formula of Duane and Laborde.

Up to the time of the present experiments a Harm's condenser was used in determining the electrostatic capacity of our electroscopes. Its capacity factor of 42.5 cms. was furnished by the makers and was accepted without verification. In the present investigations a standard condenser[14] of variable capacity with certified values by the German Reichsanstalt was kindly loaned us by the Department of Physics.

Three types of electroscopes widely used for determining radium by the emanation method were standardized with known quantities of radium emanation separated from analyzed samples of pitchblende. The electrical constants of the instruments were determined and the dimensions of the ionization chambers taken in order to deduce their respective volumes and internal surface areas. From the combined data we have computed the ionization current per curie of emanation at the time of maximum activity in the three types of instruments (1) from direct measurements and (2) by applying the formula of Duane and Laborde.

The three electroscopes used in the tests were of similar design in two respects: (1) the ionization chamber and electroscope proper are separate compartments and (2) the ionization chamber

[13] Schlundt & Moore, Radioactivity of the Thermal Waters of Yellowstone National Park, Bull. 395, U. S. Geological Survey.

[14] Physik. Zeit., 5, 294 (1904).

of each is cylindrical in form. The new interchangeable emanation electroscope[15] designed by Dr. S. C. Lind of the U. S. Bureau of Mines was chosen as one of the measuring instruments because it is widely used in laboratories where radium ores are assayed and the activity of water samples is determined, and its electrical constants have not been previously determined. Two ionization chambers of the same dimensions, but differing somewhat in electrostatic capacity, were standardized. The cylinders have air tight brass stopcocks soldered directly to the vessels in place of the glass stopcocks secured by rubber and wax connections as described by Lind. The central electrode and leaf system were both firmly mounted in amber cylinders 1.2 centimeters in diameter and 1.5 high instead of the insulation of sealing wax. In this way displacement of the electrode or leaf system is greatly minimized. The greater electrostatic capacity of Chamber No. 1 is largely due to a longer electrode which extends above the chamber in the brass cap made longer for the attachment of a screw cup to hold metallic sodium for drying the exterior surface of the insulation. The cylindrical electrodes are 0.4 cm. in diameter and extend into the chamber a distance of 8.4 cm. The other constants of the instruments are given in Table II. Instrument No. 2 is the standard form.

The second type of instrument calibrated was the quartz fiber electroscope designed by Wulf.[16] The distinctive feature of the instrument lies in the two insulated platinized quartz fibers that repel each other when they are charged. The distance between the fibers is measured by a reading microscope, and is proportional for most part of the scale to the potential to which they have been charged. The heavy base of the ionization chamber has a circular depression 2.4 cm. deep and 5.5 cm. in diameter. The central electrode is mounted in amber and is 9.4 cm. high and 0.5 cm. in diameter.

The Mache-Meyer fontactometer[17] was the third instrument used. Its ionization chamber had the relatively large volume of 14 liters. The central electrode is 25 cm. long and 0.5 cm. in diameter. The fontactometer has been widely used especially on

[15] Jour. Ind. Eng. Chem., 7, 406 (1915).

[16] Physik. Z., 8, 246; 10, 251 L'Electrometer Bifilaire et ses Applications. P. T. Wulf (Paper presented before the Scientific Society of Brussels, 1910).

[17] Phys. Zeit., 10, 860 (1909).

the continent of Europe for determining the activity of natural waters.

THE ELECTROSTATIC CAPACITY OF THE ELECTROSCOPE.

As a source of potential for calibrating the scales of the electroscope in volts per division, two boxes of dry batteries, each containing 50 batteries of three cells each and five sets of standard cells each consisting of 20 Weston elements, were used. The three sets furnished potentials up to 500 volts. In calibrating, one terminal of the batteries was connected to the case of instruments which was earthed, and the other pole was connected to the insulated electrode with sufficient batteries to bring the leaf on the scale. The potential was then increased by steps of approximately ten volts and the corresponding scale readings noted until the end of the scale was reached. By plotting volts against scale readings a curve can be drawn from which potentials corresponding to any scale readings are readily obtained. The calibration curves of the Lind and Wulf instruments were straight lines over the range of scale used in standardizing the electroscopes. The curve for the fontactometer deviates from a straight line, one division of the scale readings representing less volts as the potential increases.

In order to accurately calibrate the scales of the electroscopes, the potential of the charging batteries was determined, not by direct voltmeter readings, but by means of the Clark-Poggendorf method of compensating E. M. F's. By means of a Wolff pententiometer the E. M. F. of a suitable number of cells was balanced against a standard Weston cell calibrated in the Bureau of Standards, and this operation repeated until the E. M. F. of all the cells was determined.

For determining the electrostatic capacity of the electroscopes a normal condenser[18] of variable capacity and calibrated by the Physikalische Reichsanstalt was used. The method of Harms[19] was followed, which consists in determining first the joint capacity of the electroscope and condenser, and then the single capacity of the instrument by proper division of a known charge between the condenser and the electroscope. A detailed description of the

[18] Phys. Zeit., 5, 294 (1904).
[19] Phys. Zeit., 5, 47 (1904).

method is given by Harms and by Randall.[20] The values found for the electrostatic capacities are recorded in Table II.

STANDARD SAMPLES OF RADIUM EMANATION.

Two samples of finely ground uraninite were used as a source of radium emanation. The uranium content of one sample was determined by Randall,[21] who used it for calibrating electroscopes in terms of the Boltwood standard. The air-dry material contains 53.03 percent of uranium and 1.765×10^{-7} g. radium per gram. Since its emanation power is 2.6 percent, the emanation per gram is 1.719×10^{-7} curies, or 1.719×10^{-10} curies per milligram. The other source of emanation was a small sample of uraninite kindly furnished by Dr. Lind. It was taken from the stock sample used in the U. S. Bureau of Mines for calibrating electroscopes. According to the analysis of Lind and Whittemore[22] it contains 69.4 percent of uranium and under ordinary conditions continuously gives off 2.7 percent of the emanation produced. One milligram contains 2.10×10^{-10} curies of emanation. The quantity of uranium in a given sample multiplied by 3.33×10^{-7}, the equilibrium rate of radium to uranium, represents its radium content.

For standardizing the electroscopes known quantities of emanation were separated by dissolving weighed amounts of mineral (about 50 milligrams) in nitric acid and collecting the liberated gases mixed with air, quantitatively over hot alkaline water contained in a special form of gas burette.[23] Readings of the discharge rate of the electroscopes were always made three hours after the introduction of the emanation into the ionization chambers. Before taking a set of ten readings the electroscope was kept charged for 15 minutes.

When readings are made at the time of maximum ionization by charging the electroscope and then noting the rate of discharge at once, the successive readings generally show a slight and gradual decrease in the rate of discharge during the first ten minutes of observation, the electroscope having been left discharged since the

[20] *Loc. cit.*, p. 483.

[21] Randall, *loc. cit.*, p. 471, and in Bull. No. 70, U. S. Bureau of Mines.

[22] Jour. Amer. Chem. Soc. (1914).

[23] The apparatus for this purpose was devised by Schlundt and Moore and is described and figured in the Jour. Phys. Chem., 9, 320 (1905), also by Randall, *loc. cit.*, p. 471 and in Bull. No. 70, U. S. Bureau of Mines.

introduction of the emanation. After ten minutes the readings become quite regular. Keeping the electroscopes charged then for 10 to 15 minutes before making readings insures more accurate results. Some investigators prefer to keep the electrode charged during the entire period of three hours, thus insuring a quantitative deposition of the active deposit on either the walls of the chamber or the electrode, according as the charge on the electrode is positive or negative. The readings by both methods are quite constant, but are the ionization currents the same? This point was tested by calibrating ionization chamber No. 1 of the Lind instrument in four ways: In one series of experiments the readings were made after the electrode had been charged negatively for 15 minutes; in the next series, the charge was positive, 15 minutes; in the other two series the electrode was kept charged during the entire three hours. Ten readings were taken and averaged in each determination, and each series consisted of three determinations. The results are recorded in Table I and point to a slightly lower rate of discharge when the electrode has a three-hour positive charge. These experiments were not extended to the other types of electroscopes.

TABLE I.

Discharge Rates for Different Ways of Making Readings.

Electrode Charge	Curies of Emanation per div. per sec. X 10^9
15 minute negative	9.97
15 minute positive	9.97
3 hour negative	9.92
3 hour positive	10.22

An Example: The method of computing the calibration constant of an electroscope will be illustrated by an example. The emanation was separated from 52.5 milligrams of the Randall sample of standard pitchblende and introduced into ionization chamber No. 2 of the Lind electroscope. The quantity of emanation thus obtained is 9.03×10^{-9} curies. Ten readings taken at the time of maximum activity averaged a fall of 50 divisions of the leaf in 46.6 seconds. Hence the instrument is discharged at the rate of 1.073 divisions per second. Since the natural leak of the electroscope taken shortly before the introduction of the gas is 0.007 divisions per second, the ionization due to the emanation

is 1.066 divisions per second. Hence a fall of one division per second represents 8.47×10^{-9} curies or grams of radium. Since the electrostatic capacity of the chamber (see Table II) is 6.74 cm. and one division represents 1.14 volts, we find by substitution in equation 1, that the ionization current per curie is given by

$$\frac{6.74 \times 1.14 \times 1.066}{300 \times 9.03 \times 10^{-9}} = 3.03 \times 10^{6} \text{ e. s. units}$$

EXPERIMENTAL DATA.

The essential experimental data are given in the following table. The ionization currents are expressed in electrostatic units per curie of emanation measured three hours after the introduction of the gas. The next to the last column of the table contains the ratios of the currents measured and the values computed by the formula of Duane and Laborde for maximum ionization. The values for the ionization efficiency in the last column represent the ratio of the observed currents to the theoretical value 6.3×10^{6} e. s. units. The large and small ionization chambers used by Duane and Laborde have been included in the table and one of the rectangular electroscopes calibrated by Randall. Electroscope No. 5 calibrated by Randall has a cylindrical ionization chamber mounted above the compartment containing the leaf system. The design of the rectangular instrument differs fundamentally from the other types. Instead of separate compartments for ionization chamber and electroscope, the leaf system is contained within the ionization chamber. In computing the volume of the chambers the volume of the electrode was deducted from that of the vessel and the surface of the electrode was added to the interior surface of the chambers. The calibration data for the fontactometer represent the average of 12 determinations; for the Lind instruments nine were made with each of which the highest value was 3.12×10^{6} and the lowest 2.98×10^{6}, for chamber No. 1, the average being 3.06×10^{6}. With chamber No. 2 the highest value was 3.07 and the lowest 2.96×10^{6}, average 3.03×10^{6}. The emanation for these calibrations was obtained from the Randall sample of uraninite. The average of three determinations based upon the standard uraninite of Lind and Whittemore was 3.00×10^{6} e. s. units for chamber No. 1 and 2.92×10^{6} for chamber No. 2.

TABLE II.

Experimental Calibration Data and Computed Values.

Type of Electroscope	Height of Ionization Chamber, cm.	Diameter cm.	Volume c.c.	Interior Surface Area sq. cm.	S/V	Electrostatic Capacity, cm.	Maximum Current Per Curie E. S. Units x 10^6	Current Calculated	I Found / I Calc.	Ionization Efficiency Percent
Lind No. 1...	9.68	8.57	557	387	0.695	7.95	3.06	3.80	0.805	49
Lind No. 2...	9.68	8.57	557	387	0.695	6.74	3.03	3.80	0.80	48
Wulf Qtz. Fiber	10.1	12.1	1,216	669	0.550	3.36	3.36	4.32	0.78	53
Fontactometer	29.8	24.8	14,395	3328	0.231	10.4	4.47	5.47	0.82	71
D. & L. Large	37.5	12.5	10,057	2818	0.279	....	5.30	5.31	1.00	86
D. & L. Small	12.5	6.7	740	344	0.782	....	3.48	3.49	1.00	56.5
Randall No. 4. (Rectangular)	14.2x10.3 x6.5	..	950	630	0.663	10.7	4.46	3.92	1.14	71
Randall No. 5.	19.6	13.6	2,830	1178	0.416	14.8	4.46	4.81	0.93	71

CONCLUDING REMARKS.

With the exception of the rectangular electroscope used by Randall the measured currents have lower values than are computed by the formula of Duane and Laborde; and for our electroscopes the measured values are from 18 to 22 percent lower. The higher ratio for the rectangular instrument used by Randall may be due only partly to the form of the instrument. The fact that the front and back sides were plate glass not covered with wire gauze may have resulted in a very uneven distribution of the active deposit over the inner surface which would cause variations in the ionization currents.

The experimental results show that the reduction factor in the formula of Duane and Laborde has specific values for ionization chambers of the dimensions used in our experiments. In order then to convert curies into e. s. units or Mache units a reduction factor must be determined for each of these instruments, and the same is true if one desires to translate activities expressed in electrostatic or Mache units into curies or gram-seconds of radium. We hope that the custom of expressing activities of water and gas samples in terms of Mache units will soon be superseded entirely by stating directly the radium content or curies per liter.

The expression (*a*) on page 369 shows that 1 curie of emanation is equal to 2.89 x 10^9 Mache units, and this is the proper conver-

sion factor for grams of radium and curies of emanation per liter to Mache units.

Finally, it may be pointed out that the ionization current measured at the time of maximum activity when expressed in e. s. units per liter of water or gas may also be converted into Mache units by multiplying by the specific factor for the instrument that will reduce the maximum current per curie to 2.89×10^9. For instance, the maximum current per curie in the Lind electroscope No. 2 is 3.03×10^6 e. s. units. Hence to convert maximum ionization currents of this instrument into Mache units, multiply by the factor $2.89 \times 10^9 / 3.03 \times 10^6$ or 9.54×10^2 and divide by the volume of water or gas expressed in liters.

Chemical Laboratory,
University of Missouri.

A paper presented at the Thirtieth General Meeting of the American Electrochemical Society, held in New York City, September 28, 1916, Mr. L. E. Saunders in the Chair.

OBSERVATIONS UPON THE ATMOSPHERIC CORROSION OF COMMERCIAL SHEET IRON.

PARTICULARLY IN REGARD TO THE INFLUENCE OF COPPER AND MILL SCALE.

By E. A. Richardson and L. T. Richardson.

The corrosion of iron and steel is a question that is becoming of increasingly great importance. The problem of finding the true nature of and the ultimate causes that underlie the rusting of iron is as yet unsolved. Much work has been done in the past, is being done at present and before the problem is solved, much more will undoubtedly be done in the future.

The paper will not burden itself with a lengthy review of previous work that has been done upon the subject, but will confine itself to a brief summary of such work.

As regards the relative merits of wrought iron and steel much work has been done, but observations on the two materials seem to be in poor agreement.

Of recent years the question of the rust-resisting properties of copper-bearing steels has arisen and remains as yet unsettled, the chief contenders being the makers of copper-bearing steel and those of pure iron. As far as numerical data are concerned, the advocates of copper-bearing steel seem to be in the lead; in fact it seems to the writers that one weakness in the argument of the pure iron advocates is that they give little numerical data to support their claims. To many, their arguments would carry much more weight if such data were included.

Briefly, up to about 1910, a considerable amount of work had been done upon the subject of copper in steel, but this work was mainly in the form of fragmentary observations on steels that contained small quantities of copper either accidentally or intentionally added, and a few actual tests upon copper-bearing material. Previous to this time there appeared to be no acute controversy as to the effect of copper in steel upon corrosion,

although judging from the literature it did exist at this time to a rather mild extent as to the effect of this metal upon the physical properties of steel. The general impression, one would gain from reading these articles, is that copper in steel is a benefit as regards resistance to corrosion.

Shortly after 1910 copper-bearing steel was put upon the market as a corrosion-resisting material. The controversy then became acute, the chief objectors being the advocates of pure iron. The result has been that a considerable amount of work has been done and published without settling the question. Most of this work seems to have been done by those interested in copper-bearing steel in their efforts to prove that this material is the real rust-resisting material they claim it to be. A large share of the published work, which contains results from tests closely approaching actual service conditions, has been done by Mr. D. M. Buck[1]—a strong advocate of copper-bearing steel. The opposing side appears mostly in discussion of these and other papers and appears to be taking a defensive stand. The impression, gained by the writers, from reading the available published evidence, is that copper-bearing steels do possess rust-resisting properties and are superior to any iron or steel now on the market.

Likewise, the influence of mill-scale upon the corrosion of iron is under discussion.

Friend[2] for instance states that "traces of oxides upon the surface of metals are powerful stimulators of corrosion."

A. Sang[3] says, "Black oxide only protects provided it is continuous and firmly anchored to the iron (Bower-Barffing, etc.); as mill-scale, which is loose and fissured, it is detrimental, the iron in contact with it and exposed rusts about 50 percent faster."

Aston and Burgess[4] find "that mill-scale had an accelerating effect for an atmospheric test and a retarding action for a fume test." Further they state that "there is no doubt that the protective property of mill-scale is dependent upon its physical properties, continuity, etc."

[1] Buck, D. M. Copper in Steel—The Influence on Corrosion. Jour. of Ind. and Eng. Chem., June, 1913.
Buck, D. M., and Handy, J. O. Research on the Corrosion Resistance of Copper Steel. Jour. Ind. and Eng. Chem., March, 1916.

[2] Friend, J. N. The Corrosion of Iron and Steel, p. 251.

[3] Sang, A. The Corrosion of Iron and Steel, p. 81.

[4] Aston, James, and Burgess, C. F. The Rate of Rusting of Iron and Steel. Eighth Int. Congress of Applied Chem., 26, 453.

G. C. Whipple and M. C. Whipple[5] tested steel, ingot iron and wrought iron with mill-scale and with mill-scale removed and obtained erratic results, but, generally speaking, the rusting was slightly greater in the case of the metals from which the mill-scale had been removed than in the cases of the metals on which the mill-scale had been left. They state, however, "that the best remedy to protect steel from pitting is to remove mill-scale."

Buck and Handy[6] in their latest paper state "at the time of exposure of the full-sized corrugated sheets careful notes were taken concerning the physical appearance of the sheets as affected by the amount of mill-scale which was present, and as to whether they were outside or inside in the pack. During the progress of the test this feature was carefully watched, and the time of ultimate failure of sheets whose surfaces were comparatively free from mill-scale was compared with others of the same grade, whose surfaces were well covered with mill-scale. From these observations, we concluded that the influence of this original surface oxide is slight, and is lost in the early stages of rusting, for no difference in final failure could be noticed."

One thing, however, in regard to many tests that have been made upon the relative corrosion of iron and steel, is that insofar as the ultimate consumer is concerned, they are not of the greatest value, since many times only two or three materials were compared, or the materials were made especially for test and cannot be obtained in commercial quantities. Such tests do not carry the most weight since they do not have the air of disinterestedness that exists in the case of materials purchased upon the open market. In fact one of the arguments of the pure iron advocates is the objection to "special tests" and the demand of basing comparisons upon service tests only.

In view of the fact that no results had been published of a complete test on commercial materials, it was deemed desirable to make a test containing all the types of iron and steel that could be obtained.

Some of the kinds of materials that are commonly used for structures, exposed to atmospheric corrosion, are:

[5] Whipple, G. C., and Whipple, M. C. Mill-Scale as a Cause of Corrosion. Eighth Int. Congress of Applied Chem.

[6] Buck, D. M., and Handy, J. O. Research on the Corrosion Resistance of Copper Steel. Jour. Ind. and Eng. Chem., March, 1916.

1. Steel.
2. Puddled Iron.
3. Commercially Pure Iron.
4. Copper-Bearing Steel.
5. Cast Iron.

This paper deals with the first four classes.

Accordingly there were obtained upon the open market the following materials in the form of black sheets of 26 gauge:

1. Bessemer Steel.
2. Open Hearth Steel.
3. Charcoal Iron.
4. Commercially Pure Iron.
5. Commercially Pure Iron.
6. Copper-Bearing Iron.
7. Copper-Bearing Steel.
8. Copper-Bearing Bessemer Steel.
9. Copper-Bearing Open-Hearth Steel.

These materials analyzed as follows:

	Copper	Manganese	Carbon	Phosphorus	Sulphur	Silicon
1	Trace	0.300	0.01	0.087	0.054	....
2	Trace	0.413	0.01	0.079	0.041	....
3	0.044	0.031	0.01	0.050	0.024	0.020
4	0.016	0.028	0.01	0.009	0.025	....
5	0.028	0.009	0.01	0.006	0.024	....
6	0.237	0.006	0.01	0.004	0.054	....
7	0.181	0.100	0.01	0.003	0.027	....
8	0.256	0.315	0.08	0.092	0.046	....
9	0.268	0.387	0.01	0.052	0.024	....

Before starting a work of this character, which involved quite some labor, due consideration was given to the methods of testing and in particular to those methods about which there is some difference of opinion. Questions arose concerning the desirability of a previous heat treatment and the necessity and means of removing mill-scale previous to testing.

Opinions differ as to whether samples of iron should be tested just as received or whether all test-pieces should receive some treatment so that the physical properties will be as nearly iden-

tical as possible. One author contends that samples should be tested as purchased, since the material that the samples represent will be used just as purchased. On the other hand, there are those who contend that all samples tested should have as nearly the same treatment as possible, in order to eliminate as many of the variables as possible. They suggest, therefore, that the test-pieces be annealed at the same temperature and that mill-scale be removed.

It would seem that the method used for testing should depend upon the use to which the data is to be put. If the results are intended for the ultimate consumer the material should be tested just as purchased since this is the condition that it is used by the ultimate consumer. On the other hand, if the data is for scientific purposes such as determining the effects of various elements in the material, all variables other than the ones under investigation should be removed if it is possible to do so.

However, to make the work as broad and as complete as possible, it was decided not to limit the test to one method, but to try out both ways and to determine the relationship between the two.

Since part of the specimens were to have the mill scale removed, the question arose as to what method should be used for removing this scale. In previous published work, very little has been said about the method of cleaning test specimens. When stated, however, it has usually been done by mechanical means such as filing or grinding, or by chemical means such as acids. Experiments were, therefore, conducted on the effects of methods of removing mill-scale upon the subsequent corrosion. The results of these experiments have already been published.[7] It was shown in this paper that methods of cleaning by the use of chemicals had a profound effect upon the rate of corrosion, especially on tests of short duration.

In the contemplated test a clean iron surface was necessary in which the surface iron was in the same physical and chemical state as the iron beneath the surface. It was, therefore, decided that removal of the mill scale by pickling in sulphuric acid, thorough washing with water and drying and subsequent removal

[7] Richardson, E. A. The Effect of Pickling on the Corrosion of Iron. Met. and Chem. Eng., 12, 759.

of the surface iron with fine emery cloth would give a surface that was identical with the material itself.

The question also arose as to the method by which corrosion was to be estimated. There is a choice of methods to determine the rate of corrosion. One method commonly used is to determine the loss in weight after exposure for a given length of time and considering this loss as an index of corrosion. Another method is to allow the test specimens to corrode until failure occurs and to take the length of time as an index of corrosion. Inasmuch as there is some question as to the reliability of the "loss in weight" method, it was thought best to continue the test to the failure of the specimens.

This made it necessary to decide upon some standard condition at which failure could be considered to have taken place. Evidently, failure should not be taken at a point when the iron has completely rusted away or even when it has almost disintegrated, since any sheet iron in service would be of no value long before such a condition obtained. The point of failure selected was when the sheet iron was in such a condition that it could be seen to be perforated when the rust was removed by gentle tapping with a blunt object such as a file or nail. By using one specimen of each kind of material as a test piece that was tapped and examined at intervals of about two weeks, a close approximation to the time of failure could be obtained. Thus the other specimens were not molested until the latter part of their useful life and the effects of tapping were practically eliminated from the results. By this method, it is believed that the life of each material was obtained to within an error of three or four weeks.

The sheets of 26-gauge iron were accordingly prepared for test by cutting into pieces 5 in. x 8 in. (12.7 cm. x 20.3 cm.). For the test on the material as received ten pieces of each kind of iron, that were found by measurement to be of standard thickness, were used. For the test on the prepared material, a number of pieces of each material were annealed at a red heat and then cleaned by the method already described. Great care was taken to give all of these test pieces exactly the same treatment. Ten of the prepared specimens of each material that were found by measurement to be of the same thickness were taken for test. These prepared pieces were of practically the same thickness as

the "as received" samples tested, due, no doubt, to the extreme thinness of the mill-scale.

On account of the precautions taken as regards uniform thickness of materials, the method of estimating failure and the method of cleaning surface, it is believed that the test should be comparative.

All samples were then placed securely in a wooden rack and exposed to the weather May 24, 1914. The atmosphere was what might be described as a semi-country one, and cannot be taken as an atmospheric acid test.

At the very start a marked difference was noted in the character of the rust formed on different materials. Whereas, on the Bessemer and open-hearth steel samples, the rust was of a yellowish-red color and became loose rapidly, the rust on the others was dark red in color and much more adherent. This adherent state seemed to reach its maximum in the copper steels, where the rust was very dark and fine grained. Fig 1, Fig. 2 and Fig. 3 represent photographs taken about one year after the test was started and conveys in a rather poor way the character of the rust. Fig. 1 is characteristic of Bessemer and open-hearth steel. Fig. 2 is characteristic of charcoal iron, of commercially pure iron and iron containing copper, and Fig. 3 is characteristic of copper-bearing steels.

From visual observations at this time there appeared to be little difference between pure irons with or without additions of copper.

The life of the different materials tested is given below; each figure being an average of ten test pieces and represents the time for failure in days:

	Material As Received	Material Annealed and Surface Cleaned
1	348	363
2	367	381
3	615	558
4	598	437
5	675	467
6	743	601
7, 8, 9	1200 (estimated)	1200 (estimated)

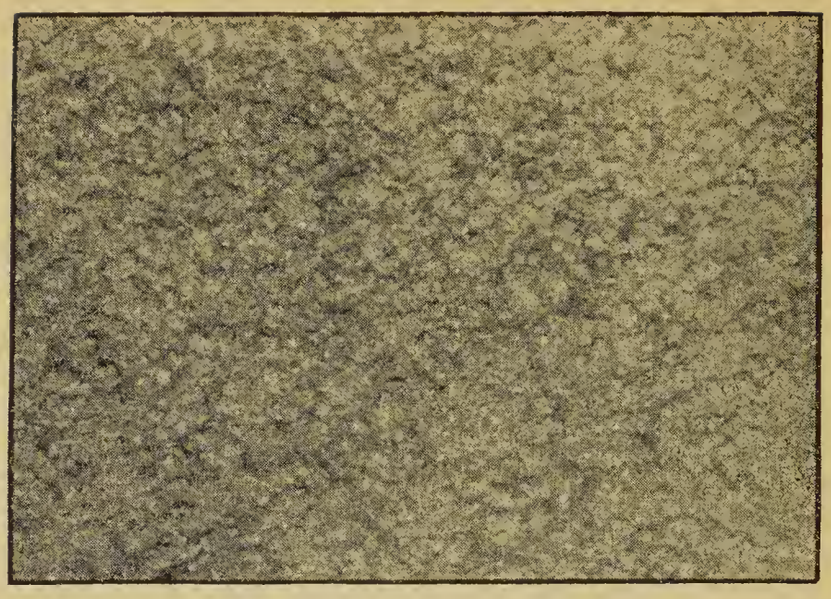

FIG. 1.

FIG. 2.

FIG. 3.

At the present writing the three samples of copper-bearing steel are still in good condition. The rust is still adherent and the underlying metal is still intact. The life of these steels have been estimated at 1200 days, which figure the writers believe is very conservative. These specimens are still exposed to the weather and will be until failure occurs.

Conclusions. Taken as a whole, the results indicate that copper-bearing steels are, without doubt, decidedly superior to any of the other materials tested. The remaining materials may be divided roughly into two classes, one class including the ordinary steels (Bessemer and open-hearth) and the other class, the commercially pure irons and the copper-bearing irons. Charcoal iron is classed with the pure irons. We have obtained results in another test which would indicate that the resistance of wrought iron to corrosion is due to the purity of its iron and not to slag inclusions. In addition, it was noted during the present test that charcoal iron appeared to corrode in very much the same way as pure iron.

In regard to the steel-iron question it is noted that the pure irons (including charcoal iron) are superior to steel. It is believed that this superiority is due to the purity of the iron, or to some combined effect of manganese and copper.

The results obtained in regard to the effects of mill-scale do not agree with the results obtained by others. They indicate that with steels which rust rapidly, mill-scale is a stimulator of corrosion. On the other materials tested, the mill-scale has exerted a protective action. We have no explanation for this.

The important feature of the results, however, is that it substantiates the claim made in several other publications that the addition of copper to steel in amounts of about 0.25 percent causes a remarkable increase in its ability to resist atmospheric corrosion. In the present test, the addition of about 0.25 percent copper to Bessemer or open-hearth steel has resulted in an increased resistance of 300 or 400 percent.

The addition of copper to pure iron also results in an increased resistance to corrosion, but to no such an extent as the addition of a similar amount to steel. The addition of about 0.25 percent copper to a commercially pure iron results in the useful life being

increased by about 20 percent. This figure was arrived at by comparing the average life of irons Nos. 3, 4 and 5 with No. 6.

We have been unable to determine the reason for this effect of copper in reducing corrosion. It is believed, in view of the fact that the copper exerts a greater influence in steel than in iron, that it must be due to the combined presence of copper and manganese, since the chief difference in the iron and steels under consideration is in the manganese content. It may be that the copper eliminates a harmful effect of manganese, or it may be that it is some combined effect of these two elements that acts as a protection to iron. The writers are inclined to believe that it is the latter cause.

This conclusion, the writers believe, is also confirmed by the results of other observers. Mr. D. M. Buck[8] tested several kinds of sheet irons and steel by exposing pieces 2 in. x 4 in. (5.08 cm. x 10.16 cm.), 27 gauge, to the atmosphere in a mill yard at McKeesport, Pa., and found the loss in weight after eleven months to be as follows:

No.	C.	Mn.	S.	P.	Si.	Cu.	Loss*	Condition of Test-Pieces After Exposure
E	.04	.30	.043	.065	....	.31	2.65	No holes.
V	.04	.39	.078	.114	....	.31	2.75	No holes.
Z	.04	.43	.049	.099	.011	.25	2.83	No holes.
D	.06	.50	.037	.016	....	.26	2.94	No holes.
C	.06	.33	.035	.018	....	.25	2.96	No holes.
H	.042	.16	.024	.003	....	.21	3.05	Few holes in 2 pieces.
O	.027	.07	.033	.007	....	.09	3.31	Few holes in 4 pieces.
W	.049	.05	.043	.005	....	.10	3.72	Many holes in all pieces.
J	.022	.03	.031	.006	....	.034	4.17	Many holes in all pieces.
I	.03	.06	.013	.052	.039	.07	4.26	Many holes in all pieces.
Y	.04	.45	.046	.099	.006	Trace	6.94	Only a lace work of steel left.

* Loss given in oz. per sq. ft.

Similar results were obtained upon tests made at Scottdale, Pa., and in McKeesport city water. These tests indicate that copper even up to 0.10 percent added to low manganese materials

[8] Buck, D. M. Recent Progress in Corrosion Resistance. Amer. Iron and Steel Inst., May, 1915.

Also pamphlet. Keystone Copper-Bearing Steel. American Sheet and Tin Plate Co.

increases their resistance to corrosion but little. Ordinary steels containing about 0.40 percent manganese, but no copper, are very poor as regards resistance to corrosion but additions of copper to such steels result in a greatly increased resistance. A maximum resistance is reached with about 0.25 percent copper. These results were also confirmed upon full-sized sheets of the same materials and in the above cited papers several excellent photographs are given.

The writers believe, in view of these results, that the resistance of pure iron to corrosion could be increased by the addition of both manganese and copper and that additions of manganese to pure iron or steel, even up to 3 or 4 percent, or more, with a corresponding increase in copper to produce a maximum effect should give a material more resistant to atmospheric corrosion than the copper steel now on the market.

Also, some interesting results might be obtained by substituting for manganese in copper-bearing steels or irons, chromium, vanadium, tungsten, or molybdenum.

SUMMARY.

1. Copper-bearing steels are decidedly superior to pure iron, steel, or charcoal iron.

2. The addition of copper to pure iron increases its resistance to corrosion, but to no such an extent as similar additions to steel.

3. Charcoal iron and pure iron are superior to steel as regards resistance to atmospheric corrosion.

4. Charcoal iron is very similar to pure iron in its resistance to corrosion.

5. Copper is believed to decrease corrosion due to some mutual influence of manganese and copper.

6. The additions of larger amounts of manganese and copper to pure iron or steel are suggested as well as additions of copper-chromium, copper-vanadium, copper-tungsten, or copper-molybdenum.

7. Mill-scale stimulates corrosion in rapidly rusting materials and retards it in slowly rusting materials.

DISCUSSION.

A. S. Cushman: The first impression this paper makes on one's mind is that it does not deal with an electrochemical problem, and it would seem to be curiously placed on the program of this Society. Discussion of this paper should come before iron and steel metallurgists who have made a special study of corrosion problems and the interpretation of corrosion tests. The paper states that the advocates of pure iron, who do not necessarily accept everything that is brought forward in the scientific and commercial exploitation of coppered steel, have failed thus far to strengthen their arguments by the publication of numerical data based on tests. Inasmuch as I have from time to time contributed to the discussion of this subject, it is proper for me to take this occasion to say that the reason I have not as yet published any numerical data is because I have been trying to prevent myself from going off at half-cock. It is my intention to wait until I get numerical data in sufficient quantity and of such a nature that when it is published it will bear analysis and will make a fair impression on the scientific and engineering world.

I have had under very close observation for over four years nearly a thousand full-size commercial sheets of 26 and 16 gauge material, including all types of iron and steel that the market affords, as well as a great number of types specially manufactured for investigation. This paper claims that the average life of 26-gauge material, when exposed to semi-rural atmospheric conditions, is about 1200 days. Our tests, located at a manufacturing center, are over 1400 days old and up to the present time comparatively very few of the competing test sheets have even shown signs of failure.

This paper draws some conclusions which I consider quite unjustified on the basis of any experimental data presented. The authors announce that whereas a small fractional percentage of copper improves the corrosion resistance of steel, it is quite inert when added to iron. This is the first time such a claim as this has ever been made, and it would require much more conclusive evidence than the paper presents to support such a contention. All of the conclusions are based on an exposure to semi-rural

atmospheric conditions of a limited number of small test pieces about 5 x 8 inches (13 x 20 cm.) in size, for a period of some 1200 days. As the result of many tests and investigations which have been made under my observation for a number of years, I do not believe that the presence or absence of copper in either iron or steel is a prime factor in corrosion resistance under the varied conditions of service and exposure. I believe that the future will demonstrate that care in manufacture, which includes such factors as soundness, homogeneity, purity, density, and, above all, efficient degasification, will be found to satisfactorily explain the wide variation in quality which service tests uncover between different types of metal.

G. Wesley Austin, an English investigator, electrically melted various kinds of iron and steel in vacuo, and in a paper presented before the British Iron and Steel Institute showed that the higher the carbon content of the steel the larger the amount of evolved gases. In a recent paper before the same Society, Sir Robert Hadfield and Dr. Friend have published a series of corrosion tests, from the results of which they conclude that low carbon and manganese are essential where high resistance to corrosion is desired. Dr. W. T. Stead, a very distinguished investigator of iron and steel problems, in the discussion of the Hadfield-Friend paper, states that copper-steel mine cables had been successfully used in cases in which the waters were very distinctly acid. On the other hand, the same wire cables of the same copper content did not give any better service than ordinary steel in other mines where the waters were not acid. Other investigators who have tried out copper-steel in competition with ordinary steels, where the conditions were alkaline, such as are found in the soil conditions in Texas and other Western States, have not found them to be superior to ordinary steels, and in many cases the reverse condition has been reported.

Taking the matter, therefore, as it stands today, and considering all the evidence that has been brought forward both for and against copper as a preservative for steel, I am more than ever convinced that other factors come into the problem which are much more important than the mere presence or absence of copper. I hope soon to be able to publish some data which will show to what extent the gas content of various types of metals affects the

quality of slow rusting or corrosion resistance. The fact, as has been shown, that it is easier to degasify high purity material than it is to degasify higher carbon and manganese steels, is only another argument in favor of purity, soundness, and homogeneity in the manufacture of metal which from its nature must be called upon to withstand severe corrosive attack when placed in service. The only criticism that I have to offer on the paper under discussion is that entirely too sweeping conclusions are drawn on the basis of the data presented.

D. M. Buck: I have read the paper by Messrs. E. A. and L. T. Richardson, and have also listened to Dr. Cushman's discussion of it with a great deal of interest.

It has been the speaker's privilege to have under his supervision during the past six or seven years a large number of exposure corrosion tests of sheet metal. One test recently completed consisted of approximately 700 full-size corrugated sheets, comprising about 25 different analyses of steel and so-called "pure irons." Previous to this time several other similar tests had been conducted, and in all I have used many thousand sheets in my experiments.

The results of these tests are a matter of record and are different from those which Dr. Cushman obtained, both in the matter of time failures and in the influence of the copper content. I find in three different characters of atmosphere complete failures in a much shorter time than has been mentioned by Dr. Cushman. Several times bessemer sheets, and in a few cases open-hearth sheets (in each case carrying only a trace of copper) failed in less than one year.

I have also found that without exception steels which contain copper will greatly outlast similar steels carrying only the usual trace of copper. I do not mean to say that I can take a carelessly-made heat of steel and by the introduction of copper make it into a high-grade product. But I have found that every heat of steel with which I have experimented has been greatly improved by the introduction of a small amount of copper.

I wish to refer to one statement made by Dr. Cushman. He said that pieces in the Richardson test were probably removed and cleaned during the progress of the test, thus introducing

factors naturally different from actual service conditions. I notice on page 248, about two-thirds way down the page, it states: "By using one specimen of each kind of material as a test piece that was tapped and examined at intervals of about two weeks, a close approximation to the time of failure could be obtained. Thus the other specimens were not molested until the latter part of their useful life, and the effects of tapping were practically eliminated from the results." I take it, therefore, that all of the heats but one in each grade which was used for tapping purposes were exposed in their original condition until the finish of the test.

There is one other point to which I wish to call attention, on page 246, where we find a table giving the chemical analyses of the various grades used in the test. It seems to me that there has either been a typographical or chemical error in reporting some of the carbon results. The carbon in open-hearth or bessemer steel is rarely, if ever, as low as 0.01, even in an annealed sheet. It will average from 0.05 to 0.15.

Considering the summary of the Messrs. Richardson's paper, it has been my experience that pure iron containing copper will outlast those carrying the usual trace, and that copper is a distinct benefit, from a corrosion standpoint, to pure irons as well as to steel.

J. W. Richards: The second conclusion of the paper is: "The addition of copper to pure iron increases its resistance to corrosion, but to no such extent as similar additions to steel." Do you agree with that?

D. M. Buck: Since I am not in position to manufacture the so-called "pure irons" and test them by various copper additions, the same way as I have done with normal steels, it has been necessary for me to draw my conclusions from materials purchased in the open markets, so in considering the behavior of such "pure irons" with and without copper, it is my opinion that copper additions are almost as beneficial to "pure irons" as to steel.

Dr. Cushman has stated in his discussion that it is his belief that as low an amount of copper as 0.03 or 0.04 present is not a benefit to steel. The conclusions of the work which has been under my observation point strongly to the fact that as little copper as 0.03 is a distinct benefit in protecting the sheets under

atmospheric conditions. It seems almost inconceivable, and was so to me at the start. So much data has, however, come to my notice in that connection, that I am firmly convinced it is a fact.

A. S. CUSHMAN: We have under test numerous sheets of steel and pure iron containing varying copper contents, beginning with practically no copper and running up by steps to as high as 1.5 percent. The corrugated full-size sheets are under exposure side by side on the same rack. They have been examined by many people, many of whom are quite unbiased observers, and in no case yet have I been able to get an opinion that up to the present time there was any reason to believe that the steels and iron containing no copper presented any different appearance from those with the higher copper content. This Society may be interested in learning that at my original suggestion, Committee A-5 of the American Society for Testing Materials has undertaken to study the question of atmospheric exposure tests and subject it to unbiased and systematic trials in three different parts of the country selected to represent sea air, a manufacturing district, and rural conditions. This program has since been carried out at tremendous cost of time, trouble and money. The test frames are just about to be erected, and will contain a great many hundreds of full-size corrugated sheets of all types.

When these tests are completed and reported, we shall know at least something about the value of atmospheric exposure tests, although we may still be left in doubt as to whether the various conditions of service exposure would yield similar results. A certain conservatism in interpreting tests is always desirable, especially when dealing with so complex and difficult a subject as corrosion resistance.

D. M. BUCK: The last speaker referred to the corrosion test being conducted by the American Society for Testing Materials. It is expected that this test will be started within the next few weeks.

It is true that I am a partisan, inasmuch as I am employed by a company manufacturing products containing copper. Dr. Cushman is also a partisan, being connected with a manufacturer of pure irons, and a large part of the available data so far published on corrosion subjects is more or less partisan in its nature. I,

therefore, will look forward to procuring definite data from the results which will be obtained in the official tests of the American Society for Testing Materials, and these tests should go a long way toward a settlement of the question as to whether or not copper additions to steels and irons are beneficial.

JAMES AUPPERLE: There seems to be quite a difference of opinion among those present today about the influence of a small amount of copper. The authors of the paper state that they can see no beneficial effect up to 0.10. Others have said they can see a difference when the copper is as low as 0.03 and 0.04. My own experience, covering a period of several years, teaches me that I cannot tell the difference between 0.03 or 0.30 copper, taking into consideration the color of the rust, or the texture of the rust, or any other conditions on which conclusions can be based.

The authors of the paper have drawn their conclusions from unwarranted data. In the first place they do not manufacture steel. They do not know what kind of material they are testing. They claim that they have tested bessemer, open-hearth and other grades of steel, but how do they know they have tested those steels? Chemical analysis will not prove it. The authors state that they purchased this material on the open market and it seems to me they are taking too much for granted when they assume the metals they test are made by a certain process.

In summing up the results of certain experiments on corrosion, Prof. Leslie Aitchison, of Sheffield University, England, states that steel containing 0.48 copper corroded more rapidly in fresh water, salt water and dilute acid than steel low in impurities and containing but a trace of copper. The Messrs. Richardson have shown pictures of the texture of rust. I have under observation thousands of sheets that have been exposed to the atmosphere for several years, and I cannot tell the difference between steel containing but a trace of copper and that which contains 0.2 or 0.3 percent.

The analytical data which the Messrs. Richardson have furnished is very incomplete. In the first place, no account has been taken of the gas content of the materials which have been tested. I have found ten times as much gas in steel which corroded rapidly as in material which stood up satisfactorily.

I have also had under observation material that contained ten times as much copper as other sheets. The high copper sheets which failed contained excessive amounts of nitrogen and carbon monoxide gases. The conclusions these authors have drawn from their experiments are not warranted.

C. G. FINK: In listening to the interesting discussion of Dr. Buck, the fact is emphasized that we do not possess any standard corrosion tests for determining the value of any particular steel. There ought to be some such standard test as the salt-water spray test. Furthermore, when we talk about exposing an iron sheet to atmospheric corrosion, we ought to state what kind of an atmosphere this is, whether a dry atmosphere or whether the atmosphere is that of a town located on the water front, or the atmosphere of a town in a manufacturing district. I am quite certain that if we exposed a steel in Pittsburgh we would get results different from those if we tested the steel in the woods of Canada. It seems very essential to me that we adopt a series of standard corrosion tests, otherwise it is impossible to compare our results.

A. S. CUSHMAN: If there was such a thing possible as a standard test that we could all agree on and that we would be willing to abide by, it would be a splendid thing. But, as I have tried to point out, corrosion is a complex problem into which a number of factors enter. These factors may sometimes be all pulling the same way, but sometimes the factors push or pull in opposite directions, so that perplexing and sometimes very unexpected results are obtained. I believe, for instance, that it is possible that a metal which would stand up very well under an atmospheric exposure test might go to pieces very quickly in sea water, or under boiler or pipe-line conditions, or when buried in earth which in one case may present an alkaline condition and in another an acid. Therefore, when it comes to proposing a standard test for corrosion resistance, I do not believe that such a thing can be found. I can only reiterate my belief that the problem begins in the furnace where care in the manufacture to produce soundness, homogeneity, purity, and proper degasification, is the real measure of high-quality material, whether it is to be used to resist corrosion or for any other purpose whatsoever.

D. M. Buck: I quite agree with Dr. Cushman as to the impossibility of producing every piece of steel or iron like every other piece, and because of that fact I have endeavored in all of my tests to eliminate that factor by using sheets from many different heats of steel. That practice has been adopted in assembling the sheets for the official test above mentioned. I believe the tests will be conducted in three characters of atmosphere; one near the seacoast at Annapolis, Md.; one in Pittsburgh, where there is considerable smoke in the air; and one in a rural district, probably a few miles outside of Chicago, at Fort Sheridan. All of the tests will be located on United States Government property.

I would like to ask Mr. Aupperle, why, in his opinion, the conclusions drawn by the Messrs. Richardson, with reference to influence of copper were not justified, when he states in his discussion that he has found that the failure of certain sheets has been due to gases. How can he draw the conclusion that a certain failure is due to gas when one other man's conclusion, based also on experience, is not justified.

James Aupperle: I drew my conclusions from chemical analysis of the material tested. I had the material analyzed under my personal supervision, and I believe the methods employed for determining gases, both nitrogen and carbon monoxide, have been gone into to a greater extent in our laboratory than any other laboratory in the world, and when I stated that steel has failed on account of the gas, I did not wish to limit it to nitrogen gas. I have also tested steel which contains ten times the carbon monoxide of other material, which has stood up satisfactorily.

The Messrs. Richardson draw their conclusions from analytical data, which Mr. Buck himself criticises, the carbon, for instance, in stating this as 0.01 when it should be 0.10, and he also stated that it is unusual for the carbon to run that low.

I think from the analytical data I have I was justified in drawing my conclusions and owing to the lack of analytical data the authors are not justified in drawing their conclusions.

W. H. Walker (*Communicated*): The authors have here added another series of experiments to the many now recorded in scientific literature which show that no other type of commer-

cial iron or steel withstands atmospheric corrosion so well as does good steel which contains about 0.25 percent of copper. It is peculiarly fitting that such a paper be presented to this Society, for the reason that corrosion is an electrochemical phenomenon, and it is to the electrochemist that we must finally turn for a scientific explanation of the wonderful effect which this relatively very small amount of copper unquestionably has. As has been the case in the development of most fundamental conceptions, the electrolytic theory of corrosion has been both helpful and harmful. It has helped us to understand the factors which influence corrosion of the metals, and has led to many useful applications. On the other hand it hindered progress somewhat by indicating that homogeneity of structure, through elimination of differences of potential, would in itself retard normal corrosion, while heterogeneity would in itself insure rapid corrosion. Experience has shown us that such is not the case. The electrolytic theory failed to predict, and has not yet offered an explanation for the marked retarding influence of copper in steel upon its atmospheric corrosion. It is by bringing such papers as these before the Society that an interest in the scientific explanation of the phenomena described is created, and progress insured.

In the preceding discussion, Dr. Cushman enlarges the field of corrosion considered far beyond that assumed by the authors, and yet finds fault with their conclusions in that they are too sweeping. The paper has to do only with atmospheric corrosion, and the conclusions refer, of course, to exposure under these conditions. Dr. Cushman introduces conditions which vary from mine water containing acid, to Texas soil containing alkali—conditions which, as I understand the paper, the authors do not consider. Dr. Cushman's statement, that he cannot agree with the authors, inasmuch as in his tests he finds no difference in appearance between iron and steel containing copper and that containing no copper, is so surprising as to deserve comment. I have seen many comparative tests carried on in widely different parts of the country by perfectly independent experimenters, always with the results described in this paper. The last one observed was a large scale test of commercial size sheets, exposed by a jobber in sheet metal, for his own information. He selected the sheets, six of each brand, at random from his large stock and observed the necessary

precautions to insure equality of treatment during exposure. In this test, as in every other which I have observed, without exception, the results were practically those here reported; in each and every case the appearance of the sheets containing copper is markedly different from the others. With copper the rust is very dark brown and closely adherent; while on sheets containing no copper the rust is yellowish red and in loose particles. The difference is even much more marked than is indicated in the photographs shown in this paper.

E. A. Richardson (*Communicated*): It is rather unfortunate that the discussion of this paper or rather the criticisms of the article and the conclusions are of such a general nature and worded in such a manner that it is almost impossible to make a reply. The various criticisms are, in fact, merely statements of opinions without numerical data or observations. Until such data is included, there is nothing tangible to argue about. When Dr. Cushman's long-heralded paper on the influence of gas content appears we may be able to discuss the subject more intelligently.

There were, however, one or two statements made, that can hardly be left unanswered. Mr. Aupperle states that "The authors of the paper state that they can see no beneficial effect up to 0.10 percent (copper)." Evidently, Mr. Aupperle could not have read very thoroughly the article he is attempting to discuss, for our second conclusion says, "The addition of copper to pure iron increases its resistance to corrosion, etc."

The same gentleman also thinks that our data are unwarranted, since the materials tested were purchased in the open market and that we, therefore, did not know what kind of materials we were testing. We can only say that in any test (even if conducted by Mr. Aupperle himself) one must, when the final analysis is made, accept the word of others and assume it to be the truth. We purchased our materials from a reliable jobber of established reputation, in some cases shipment being made directly from the manufacturers. Furthermore, each brand was checked by analysis. As Mr. G. H. Clevenger has stated in a somewhat similar discussion on copper steel, "Let us not befog the issue with suppositions of this kind, but rather deal with the problem in the broad manner which its importance deserves."

Inasmuch as there seemed to be some question as to the carbon content of the open-hearth and bessemer steels tested, we have had them again analyzed with the results as follows:

Copper bearing Bessemer	0.022	percent
Copper bearing open hearth	0.017	"
Bessemer	0.020	"
Open hearth	0.018	"

These determinations were made by the combustion method, whereas the percentages given in the paper were obtained by the color comparison method.

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